On the Catalytic Action of Japanese Acid Earth. XIII*. The Catalytic Action on Some Alkyl Aryl Acetaldehydes.

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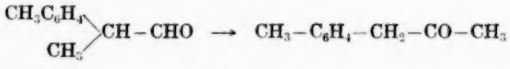
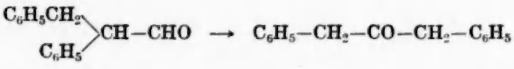
In the previous papers it was reported that some diarylacetaldehydes were converted into the corresponding ketones when heated at about 300°C. in the presence of Japanese acid earth. When this rearrangement occurs there is a possibility of the formation of either one ketone or other as the result of the migration of one of the radicals, and the author has postulated that it separates as an anion and that the more electron-attracting radical always migrates in preference to the other less electron-attracting. When the migrating tendencies of the two radicals are not greatly different, both of the radicals migrate simultaneously, giving a mixture of two isomeric ketones. The yields in the two ketones depend upon the migrating tendencies of the two radicals, which are determined by their capacities for electron-attraction.

Now the methyl group is generally accepted as less electron-repelling than the *p*-tolyl group[1], therefore the methyl group will migrate in preference to the *p*-tolyl if methyl p-tolyl acetaldehyde is subjected to the above-mentioned rearrangement as shown below:—



Similarly, the benzyl group will be expected to migrate in preference to the phenyl group in the case of benzyl phenyl acetaldehyde. The facility of the separation of the benzyl anion must be increased, moreover, by the enhanced stability of this anion relative to phenyl.



It has been found, however, that the above mentioned two aldehydes are converted chiefly into hydrocarbons at 300°C. in the presence of the earth and the corresponding ketones have not been confirmed to exist in the reaction products. They must, therefore, be considerably more unstable than diarylacetaldehydes, described in the previous papers, and the condition of the present experiment is probably too drastic for them to undergo smoothly the usual rearrangement.

The reaction product from methyl *p*-tolyl acetaldehyde has been found to contain only about 3% of oxygen, but the aldehyde or ketones isomeric to it should contain 10.8%. Benzyl phenyl acetaldehyde gave products containing a still less quantity of oxygen. The reaction products

* This Bulletin **16** (1941), 349.

(1) H. Burton and C. K. Ingold: *J. Chem. Soc.* **1928**, 907.

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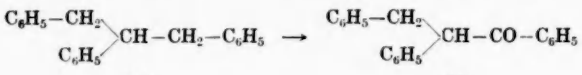
from both of the aldehydes showed no colour reaction, characteristic to aldehyde. All attempts to obtain definite forms of oximes or semicarbazones of ketones from the reaction products failed. The main products were accordingly treated with metallic sodium in order to remove the oxygen-containing substances, and then fractionated, when a mixture of almost pure hydrocarbons was obtained.

Among the reaction products from methyl *p*-tolyl acetaldehyde, toluene and a compound $C_{10}H_{12}$, possibly $CH_3-C_6H_4-CH=CH-CH_3$ were confirmed to exist, while in the reaction products from benzyl phenyl acetaldehyde a solid crystalline substance of the composition $C_{15}H_{12}$[2] with a melting point 165–166°C. was found.

It has been found that 1,2,3-triphenylpropane (I) is produced together with benzyl phenyl acetaldehyde when *α*-benzyl *α*-phenyl ethylene glycol is heated with a mixture of oxalic acid and water at 113°C. 1,2,3-Triphenylpropane gave benzyl deoxybenzoin (II) on oxidation with chromic oxide. From this fact its constitution has been confirmed.



(I) (II)

Experimental. *α-Benzyl α-phenyl ethylene glycol.* When magnesium is allowed to react with the calculated quantity of benzyl bromide, dissolved in dry ether, as has J. Marshall[3] noticed, a large proportion of magnesium remains undissolved with the formation of a considerable quantity of dibenzyl. Pulverised benzoyl carbinol (20 g.) was added by portions to the solution of magnesium (16.4 g.) in benzyl bromide (193 g.) dissolved in ether, and the Grignard reagent thus formed was boiled for 30 hours. It was poured into acetic acid (50 g. glacial acetic acid in 300 c.c. ice water) and the upper layer of the reaction mixture was treated as usual, giving a yellowish liquid (ca. 300 c.c.), from which separated a large amount of dibenzyl. It was filtered and the filtrate was distilled in steam and further amount of dibenzyl (ca. 40 g. in total) passed over. The contents of the distilling flask were cooled and a part of *α*-benzyl *α*-phenyl ethylene glycol separated out in flocky precipitate while the main part of the glycol settled down at the bottom in viscous oily mass (30 g.).

The precipitate was recrystallised from ligroin into fine needles, m.p. 79–80°C. (Found: C, 78.9; H, 7.3. $C_{15}H_{16}O_2$ requires C, 78.9; H, 7.0%). The viscous oil solidified only when innoculated with crystals of the glycol. The monobenzoyl drivative of the glycol was obtained by Schotten-Baumann's method. It formed a viscous matter, which solidified when rubbed with a glass rod with the addition of a small quantity of alcohol. It was recrystallised from dilute alcohhol into fine needles, m.p. 100.5–

(2) Ramart and F. Salmon-Legagneur (*Bull. soc. chim.*, **45** (1929), 478) obtained a substance of the composition $C_{15}H_{12}$ by passing *α*-benzyl *α*-phenyl ethylene glycol over diatomaceous earth heated at 500°C. Though its chemical and physical properties are not described at all, it may probably be identical with the substance obtained by the present author.

(3) *J. Chem. Soc.*, **107** (1915), 520.

101.5°C. (Found: C, 79.6; H, 5.9%; Mol. wt. (Rast), 335.1. $C_{22}H_{20}O_3$ requires C, 79.5; H, 6.0%: Mol. wt., 332).

Oxidation of α-benzyl α-phenyl ethylene glycol to desoxybenzoin. Chromic oxide (0.31 g.) was added to the solution of the glycol (0.3 g.) dissolved in 70% acetic acid (50 c.c.) and the solution was heated on the water bath for 4 hours and poured into a large amount of water. White crystals separated out, which formed colourless scales (0.15 g.) from dilute alcohol. It melts at 57–58°C. alone or mixed with the authentic specimen of desoxybenzoin.

Benzyl phenyl acetaldehyde. A mixture of α-benzyl α-phenyl ethylene glycol (60 g.), crystalline oxalic acid (150 g.) and water (60 c.c.) was heated in an oil bath for 4 hours at 113°C. The reaction mixture was treated as usual and distilled under the reduced pressure of 4 mm., giving the following fractions:—

Table 1.

Fraction	B. p. (°C.)	Yields (in g.)	Remarks
(1)	Below 172	1.0	—
(2)	172–175	7.5	—
(3)	175–205	13.8	Boiling mainly at 202–205°C.
(4)	Residue	—	—

The fraction (2) in Table 1 consisted of the required aldehyde, d_4^{22} 1.0684; n_D^{22} 1.5861; M. R. found, 65.96; calc. (Eisenlohr), 64.28. The semicarbazone was produced with difficulty; after standing for 5 days the mixture of the aldehyde (1.0 g.), semicarbazide hydrochloride (1.0 g.) and potassium acetate (1.0 g.) dissolved in dilute alcohol, a large amount of water was added to the solution. The oil drops separated thereby solidified to the yellow powder (0.95 g.), which was recrystallised several times from dilute alcohol forming colourless fine needles, m.p. 123.4–124.4°C. (corr.). H. Burton and C. W. Shoppee[4] obtained the same aldehyde by reducing the corresponding iminochloride with stannous chloride and then hydrolysing the resulting aldimine. It boiled, according to them, at 170°C./11 mm., and solidified after several weeks, and on recrystallisation formed colourless plates, m.p. 54°C. and its semicarbazone melted at 124–125°C. R. Stoermer, Cl. Thier and E. Laage[5] described it as the monohydrate, m.p. 116°C., characterised by a semicarbazone, m.p. 189°C. (decomp.), which however was confirmed by H. Burton and C. W. Shoppee to be phenyl acetylphenyl carbinol. F. Kayser[6] synthesised the aldehyde by treating 1,3-diphenylpropane-(1) with mercury oxide and iodine and gave the boiling point 179–180°C./18 mm.

(4) *J. Chem. Soc.*, **1937**, 546.
(5) *Ber.*, **58** (1925), 2607.
(6) *Ann. chim.*, [11] **6** (1936), 145.

1,2,3,-Triphenylpropane. The fraction (3) in Table 1 tinged concentrated sulphuric acid with a deep red colour and contained a small proportion of oxygen. (Found: C, 91.3; H, 7.2%). It was treated with metallic sodium to remove the oxygen-containing substances, and a hydrocarbon $C_{21}H_{20}$ was obtained in colourless viscous oil, b.p. 204–205°C./8 mm.; $d_4^{30.4}$ 1.0254; $n_D^{30.4}$ 1.5864; M. R. found, 89.07, calc. (Eisenlohr), 88.38. (Found: C, 92.5; H, 7.5. $C_{21}H_{20}$ requires C, 92.7; H, 7.3%). It dissolves in concentrated sulphuric acid, developing brownish yellow colour with faint cobalt fluorescence. Its identity with 1,2,3-triphenylpropane was revealed by the formation of benzyl desoxybenzoin when oxidised with chromic oxide. E. Späth[7] obtained the hydrocarbon by allowing benzyl halide to react with methyl- or ethylmagnesium halide and gave b.p. 225–230°C./10 mm. The hydrocarbon (1.1 g.) was dissolved in glacial acetic acid (30 c.c.), and chromic oxide (3.3 g. dissolved in 3 c.c. water) was added to the solution. After completing the reaction by heating the solution on the water bath for 1 hour, a small quantity of formic acid was added in order to decompose the excess chromic acid and the acetic acid was distilled off under the reduced pressure on the water bath. The residue was a deep green mud. It turned white on washing with water, and crystallised from dilute alcohol forming pure *ms*-benzyl desoxybenzoin in fine needles (0.25 g.), m.p. 120–121°C. (Found: C, 87.7; H. 6.5%; Mol. wt. (Rast), 289 295. $C_{21}H_{18}O$ requires C, 88.1; H, 6.3%; Mol. wt., 286). The oxime obtained by Auers' method formed colourless needles, apparently a pure substance, which however melted at 116–127°C. after recrystallisation 10 times from dilute alcohol and most probably consisted of a mixture of stereo-isomers. F. Klingemann[8] obtained *ms*-benzyl desoxybenzoin by reducing *ms*-benzal desoxybenzoin and gave m.p. 120–122°C. A. Mckenzie and E. R. Winton[9] obtained it by interacting methyltropate with phenyl magnesium iodide, which melted at 120–121°C.

Attempted isomerisation of benzyl phenyl acetaldehyde. By passing 7.0 g. of the aldehyde on the Japanese acid earth (25 g.), heated at 300°C. at a rate of 3.2 g. per hour, accompanied by a slow current of carbon dioxide the following products were obtained: (a) 0.6 g. of easily-flowing oil with faint fluorescence and (b) 3.5 g. of a yellow solid mass moistened with oily substance. The product (a) consisted chiefly of toluene and benzene. The product (b) was separated into two parts, i.e., (i) crystalline mass (0.6 g.) and (ii) oily substance (2.3 g.), when it was pressed with a filter paper and the paper was extracted with ether. The product (i) crystallised from alcohol in colourless scales, m.p. 165–166°C. (Found: C,93.5; H, 6.3%; Mol. wt. (Rast), 197, 206. $C_{15}H_{12}$ requires C, 93.8; H, 6.2%; Mol. wt., 192). Attempts to obtain any compound of a definite constitution by oxidising the foregoing hydrocarbon with chromic oxide failed and its constitution was for the time left open. Ramart and F. Salmon-Legagneur[10] obtained a compound $C_{15}H_{13}$ by passing *a*-benzyl *a*-phenyl ethylene glycol on the diatomaceous earth heated at 500°C. How-

(7) *Monatschaft.*, **34** (1913), 1992.
(8) *Ann.*, **275** (1893), 65.
(9) *J. Chem. Soc.*, **1940**, 840.
(10) *Bull. soc. chim.*, **45** (1929), 478.

ever, no detailed description of properties of the compound has been given by them.

The portion (ii) was distilled under the reduced pressure of 10 mm. and 1.7 g. out of 2.3 g. passed over between 150–200°C, which contained 91.7% of carbon and 7.2% of hydrogen and may be considered to consist of 74% of $C_{15}H_{12}$ and 26% of $C_{15}H_{14}O$. It showed no colour reaction characteristic to aldehydes and formed neither semicarbazone nor oxime.

α-Methyl α-p-*tolyl ethylene glycol.* *p*-Methyl benzoyl carbinol (45 g.) was added by portions to the Grignard reagent prepared from methyl iodide (150 g.) and magnesium (24 g.) and left to stand for 2 days. It was treated with acetic acid (120 g. glacial acetic acid in 300 c.c. ice water), the ethereal layer was separated and combined with the ether extract of the water layer, the combined ethereal extract dried with anhydrous sodium bicarbonate, the ether removed and the residue was distilled in vacuo. 33 g. of the raw *α*-methyl *α-p*-tolyl ethylene glycol passed over between 150 and 158° under 33 mm. M. Tiffeneau[11] obtained the glycol by the same method and found that it melted at 36°C. and boiled at 175–180°C/15 mm. These data widely deviated from the present author's values.

p-*Tolyl propionaldehyde.* A mixture of raw *α*-methyl *α-p*-tolyl ethylene glycol (30 g.), crystalline oxalic acid (75 g.) and water (30 c.c.) was boiled gently in an oil bath for 3 hours, meanwhile a slow current of carbon dioxide was passed into the reaction flask. The reaction product was extracted with ether, washed with aqueous potassium carbonate and with water, dried over anhydrous sodium sulphate, the ether removed and the residue was distilled. 14 g. of the required aldehyde were obtained, b.p. 222–225°C.; d_4^{23} 0.9928; n_D^{23} 1.5173; M. R. found 45.12. $C_{10}H_{12}O$ (Eisenlohr) requires 44.79. W. v. Miller and G. Rohde[12] gave b.p. 222–224°C./760 mm. (corr.), G. G. Henderson and W. Cameron[13] b.p. 221–222°C./755 mm.; d_{20}^{20} 0.984; n_D^{20} 1.51436, and M. Tiffeneau,[14] b.p. 219–221°C. The semicarbazone was synthesised by the usual way forming silky needles from dilute alcohol, m.p. 155.5–156.5°C. (uncorr.). G. Darzens[15] gave m.p. 159–160°C. and G. G. Henderson[16] m.p. 156–157°C., while M. Tiffeneau[17] m.p. 152°C.

Attempted isomerisation of methyl p-*tolyl acetaldehyde.* The aldehyde (12 g.) was passed on the Japanese acid earth (25 g.) heated at 300°C. at a rate of 3.6 per hour, accompanied by a slow current of carbon dioxide and gave (a) a yellow oil (5.9 g.) mixed with a small amount of crystals and water (1.1 g.) which came out until the passing of the aldehyde ended and (b) a faint yellow resinous matter (0.5 g.). The product (a) was separated from water and distilled, giving the following fractions:—

(11) *Compt. rend.* **137** (1903), 1261; *Ann chim.*, [8] **10** (1907), 343.
(12) *Ber.*, **23** (1890), 1075.
(13) *J. Chem. Soc.*, **95** (1909), 969.
(14) *Compt. rend.*, **137** (1903), 126.
(15) *ibid.*, **139** (1904), 1216.
(16) *J. Chem. Soc.*, **91** (1907), 1874.
(17) *Loc. cit.*

Table 2.

Fraction	B. p. (°C.)	Yield (in g.)	Remarks
(1)	Below 200	2.1	Main part passed over above 180°C.
(2)	200–205	0.7	
(3)	205–230	0.9	The last 2 or 3 drops changed to mush on cooling.
(4)	Residue	1.1	Redish viscous oil containing crystals.

The fractions (1), (2) and (3) in Table 2 gave the following analytical data; C, 89.3, 88.0 and 86.7; H, 9.3, 9.2 and 8.2% respectively, suggesting that the higher the boiling point the richer in compounds which contain oxygen. The fractions (1) and (2) were combined and treated with metallic sodium in order to remove oxygen-containing substances and again fractionated as follows:—

Table 3.

Fraction	B. p. (°C.)	Yield (in g.)	Remarks
(1)	Below 110	0.6	Boiled almost constantly at 110°C.
(2)	110–180	0.4	Main part passed over above 159°C.
(3)	180–185	0.5	—
(4)	Residue	0.5	—

The fraction (1) in Table 3 consisted of almost pure toluene and the fraction (2) was found to be a compound $C_{10}H_{12}$; d_4^{26} 0.8615; n_D^{26} 1.4940; M. R. found, 44.61, calc. (Einsenlohr) for $C_{10}H_{12}$, 44.31. (Found: C, 90.4; H, 9.4. $C_{10}H_{12}$ requires C, 90.9; H, 9.1%).

The author's thanks are due to Dr. H. Inoue for his kind advice.

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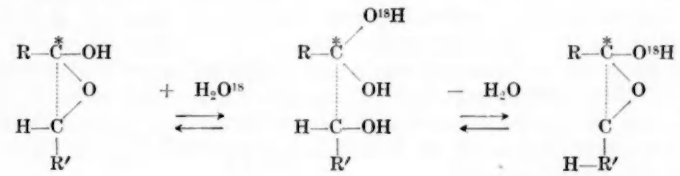
Untersuchungen der chemischen Eigenschaften der Kohlenhydrate mit Hilfe des schweren Sauerstoffs. II. Austauschreaktion und Mutarotation der Glucose und Fructose (Auszug).[1]

Von Kokiti GOTO und Toshizo TITANI.

(Eingegangen am 23, Juli, 1941).

Inhaltsübersicht. Die Geschwindigkeit der Austauschreaktion der O-Atome zwischen der Glucose bzw. Fructose und Wasser sowie die der Mutarotation desselben Zuckers in wässeriger Lösung wird unter den möglichst gleichen Versuchsbedingungen miteinander verglichen, indem man die neutrale Lösung des betreffenden Zuckers auf 30 bis 100°C., 0 bis 390 Min. lang erwärmt. Dabei wird festgestellt, dass bei 55°C. und 100°C. die Austauschreaktion fast ebenso schnell wie die Mutarotation verläuft, während bei 30°C. wo die Mutarotation noch mit wohl messbarer Geschwindigkeit ziemlich schnell stattfindet, die Geschwindigkeit der Austauschreaktion fast unmessbar so klein ist. Deshalb wird geschlossen, dass mindestens bei Zimmertemperatur der Mechanismus der Mutarotation ganz anders als der der Austauschreaktion angenommen werden muss. Als der wahrscheinlichste Mechanismus der Mutarotation bei Zimmertemperatur kommt die Prototropie in Betracht, obwohl bei hohen Temperaturen daneben noch die anderen Arten der Reaktionen, wie z. B. die Zwischenbildung der Hydrate als der mögliche Mechanismus der Umkehrung der räumlichen Struktur der Zuckermoleküle eintreten können.

Einleitung. Erwärmt man die wässerige Lösung der Glucose bzw. Fructose auf 55°C. 100 Stunden lang bzw. auf 100°C. 10 Stunden lang, so wird ein O-Atom in einem Zuckermolekül gegen die des Wassers ausgetauscht.[2] Dieser Austausch der O-Atome zwischen Zucker und Wasser wird durch die Annahme gedeutet, dass ein Wassermolekül einem Zuckermolekül umkehrbar addiert und dadurch ein Hydratmolekül intermediär gebildet wird:



Findet aber solch eine Reaktion nach beiden Seiten mit messbarer Geschwindigkeit statt, so entsteht neben der Austauschreaktion der O-Atome auch die Möglichkeit, dass die räumliche Struktur des Zuckermoleküls um das mit * bezeichnete C-Atom während der Reaktion umgekehrt und dadurch die Mutarotation des Zuckers herbeigeführt wird. Dieser Mechanismus der Zwischenbildung der Hydrate wird in der Tat als ein möglicher Fall von Lowry[3] angenommen. Wäre aber diese Reaktion

(1) K. Goto, *J. Chem. Soc. Japan*, **62** (1941), 408. Vorläufig mitgeteilt in T. Titani und K. Goto, *Proc. Imp. Acad. Tokyo*, **16** (1940), 398. I. Mittl.: dies Bulletin, **16** (1941), 172.
(2) K. Goto und T. Titani, dies Bulletin, **16** (1941), 172.
(3) M. Lowry, *Trans. Chem. Soc.* **83** (1903), 1314.

massgebend für die Mutarotation, so müsste zu gleicher Zeit der Mutarotation ein O-Atom in einem Zuckermolekül gegen die des Wassers ausgetauscht werden. Um das experimentell zu bestätigen, wird die Geschwindigkeit der Austauschreaktion und Mutarotation der Glucose und Fructose in wässerigen Lösungen unter den möglichst gleichen Versuchsbedingungen miteinander verglichen. Der Versuch ergab, dass die beiden Reaktionen bei hohen Temperaturen (mindestens oberhalb 55°C.) miteinander fast ebenso schnell stattfinden aber bei Zimmertemperatur die Geschwindigkeit der Austauschreaktion im Vergleich mit der Mutarotation unmessbar so klein ist.

Versuchsmethode und Ergebnisse. Die von Merck bezogene Glucose bzw. Fructose wird durch die Erwärmung auf 90°C. bis 100°C. in Vakuum möglichst vollständig getrocknet. Etwa 0.9 bis 1.6 g. des so getrockneten. Zuckers wird in etwa 10 bis 13 ccm. an schwerem Sauerstoff angereicherten schweren Wassers aufgelöst und auf einer bestimmten Temperatur bestimmter Zeitlänge erwärmt. Das zu diesem Versuch benutzte an schwerem Sauerstoff angereicherte schwere Wasser wird mit Hilfe der fraktionierten Destillation des Wassers hergestellt und der zu gleicher Zeit angereicherte schwere Wasserstoff auf dem schon in I. Mittl. angegebenen Wege unter Benutzung der Elektrolyse beseitigt. Der Dichteüberschuss des verwendeten schweren Wassers, der gewöhnlichem Wasser gegenüber etwa 30 γ beträgt, kann deshalb lediglich auf die Anreicherung des schweren Sauerstoffs zurückgeführt werden. Nach der Beendigung der Erwärmung wird die Lösung, nachdem sie durch das Begiessen des kalten Wassers auf dem die Lösung enthaltende Glasrohr schnell abgekühlt worden ist, in zwei möglichst gleiche Teile abgetrennt, um die erste Hälfte zur Bestimmung der Austauschreaktion und die andere Hälfte zur Bestimmung der Mutarotation zu benutzen.

Um die Austauschreaktion zu bestimmen, wird das schwere Wasser zuerst durch die Vakuumdestillation vom Zucker abgetrennt. Dabei konnten wir etwa 80% der benutzten Menge des Wassers abdestilliert wiederbekommen.[4] Der Dichteüberschuss des so abgetrennten Wassers wird, nachdem es auf passendem Wege gereinigt worden ist, genau so wie in I. Mittl. schwebemetrisch bestimmt. Die statistische Anzahl n der O-Atome in einem Zuckermolekül, die unter den angegebenen Versuchsbedingungen gegen die des Wassers ausgetauscht werden, wird dann mit Hilfe der Gl. berechnet:

$$n = \frac{M_w}{M_z} \frac{\Delta s_a - \Delta s_e}{\Delta s_e}$$

In dieser Gl. bedeutet M_w und M_z resp. die Molzahl des zum Versuch benutzten Wassers und Zuckers und Δs_a und Δs_e den gewöhnlichem

(4) Wird die Lösung gegen Ende der Destillation, wie dies bei den Versuchen in I. Mittl. der Fall war, mehr oder weniger erwärmt, so können wir mehr als 90% des verwendeten Wassers abdestilliert wiederbekommen. Da aber bei dem vorliegenden Versuche nicht nur bei erhöhter Temperatur sondern auch bei 30°C. gearbeitet werden sollte, wurde die Destillation immer bei Zimmertemperatur ohne Erwärmung durchgeführt. Die verhältnismässig kleine Ausbeute des abdestillierten Wassers wird darauf zurückgeführt.

Wasser gegenüber gemessene Dichteüberschuss des schweren Wassers vor und nach dem Versuch. Die so berechnete Anzahl n muss aber die obere Grenze von n ausdrücken, weil der schwere Sauerstoff bei der Abdestillation des schweren Wassers aus der Lösung mehr oder weniger im zurückgebliebenen Teil angereichert wird und dementsprechend der gefundene Wert von Δs_e bis zu einem gewissen Grad zu gross sein soll.

Zur Bestimmung der Geschwindigkeit der Mutarotation wird die oben angegebene andere Hälfte der erwärmten Lösung zunächst unter Zusatz des gewöhnlichen destillierten Wassers schnell bis zu 6 bis 12%ig verdünnt und das optische Drehungsvermögen der so verdünnten Lösung wird mittels eines Polarimeters bestimmt. Dabei gaben wir besonders darauf acht, dass alle diese Behandlungen so weit wie möglich schnell durchgeführt werden, um dadurch das unbekannte Fortschreiten der Mutarotation während dieser Manipulationen möglichst aufzuhalten. Das so bestimmte spezifische Drehungsvermögen $[\alpha]^D$ wird bei der Glucose ohne weiteres dagegen bei der Fructose erst nach der Korrektion für die Temperatur und Konzentration[5] in der letzten Spalte der Tabelle 1 bis 4 wiedergegeben, wo die mit * bezeichneten Werte aus den veröffentlichten Daten aufgenommen wurden.[6]

Tabelle 1. Glucose bei 30°C.

Zeit in Min.	n	$[\alpha]^D$
0	0.4	+92.2
20	0.3	+78.3
45	0.3	+64.0
45	0.3	+63.7
130	0.1	+55.3
130	0.4	+56.4
300	0.4	+52.7
390	0.4	+51.8
390	0.3	+52.7
∞	(1.0)	+52.7*

Tabelle 2. Glucose bei 55°C.

Zeit in Min.	n	$[\alpha]^D$
5.5	(0.0)	+105.2*
60	0.7	+ 64.4
120	0.8	+ 57.5
∞	(1.0)	+ 52.7*

Tabelle 3. Glucose bei 100°C.

Zeit in Min.	n	$[\alpha]^D$
5.5	(0.0)	+105.2*
30	0.9	+ 52.3
45	0.9	+ 52.1
∞	(1.0)	+ 52.7*

Tabelle 4. Fructose bei 30°C.

Zeit in Min.	n	$[\alpha]^D$
0	0.2	−104*
15	0.1	−92.2
35	0.2	−91.8
60	0.1	−92.5
∞	(1.0)	−92.1*

Zieht man die oben hingewiesene Tatsache in Rechnung, dass das in Tabellen angegebene n die obere Grenze der Anzahl der ausgetauschten

(5) Um das direkt gemessene Drehungsvermögen der Fructose zum idealen Fall umzurechnen, wo die Temperatur $t = 20°$C. und die Konzentration $c = 1$ beträgt, wird die Gl. benutzt (vgl. Jungfleisch und Grimbert, *Compt. rend.*, **107** (1888), 393):

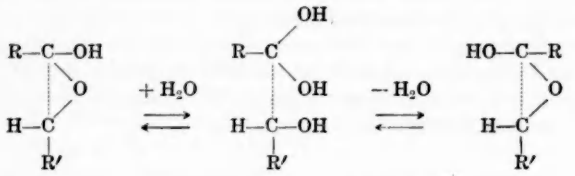
$$[\alpha]^D_{t,c} = -100.38° + 0.56\,t - 0.108\,c$$

(6) E. Parcus und B. Tollens, *Ann.*, **257** (1890), 164.

O-Atome susdrückt, so darf wohl geschlossen werden, dass bei 30°C. fast keine messbare Austauschreaktion der O-Atome zwischen jeder Art des Zuckers und Wasser stattfindet, obwohl die Mutarotation bei derselben Temperatur mit wohl messbarer Geschwindigkeit verläuft. Dagegen finden bei 55°C. und 100°C. die beiden Arten der Reaktionen der Glucose miteinander fast ebenso schnell statt.

Diskussion der Ergebnisse. Als den möglichen Mechanismus der Mutarotation sind bisher mindestens drei Annahmen vorgeschlagen worden.

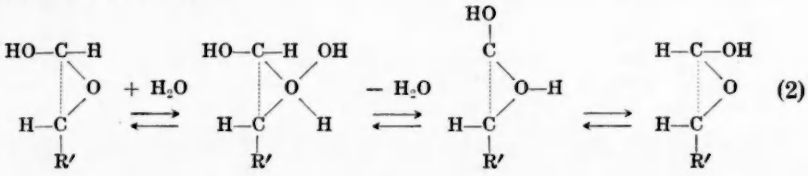
(i) Der erste Mechanismus, der von Lowry[7] stammt, nimmt an, dass ein Wassermolekül an einem Zuckermolekül addiert und das dadurch gebildete Hydrat wieder in Wasser und Zucker gespaltet wird:



(1)

Die Umkehrung der räumlichen Struktur des Zuckermoleküls wird durch diese umkehrbare Bildung und Spaltung des Hydratmoleküls herbeigeführt.

(ii) Der zweite Mechanismus, der von Armstrong[8] vorgeschlagen wurde, nimmt ebenso wie der erste die Zwischenbildung eines Hydratmoleküls an. Aber in diesem Fall werden die OH-Gruppe und das H-Atom des addierenden Wassermoleküls beide am Pyranring-O-Atom angelagert und aus dem so gebildeten Hydratmolekül wird eine OH-Gruppe vom Pyranring-O-Atom, hingegen ein H-Atom vom Carbonylkohlenstoffatom abgerissen, um ein Wassermolekül zu bilden, so dass ein H-Atom am Pyronring-O-Atom zurückgelassen wird, das eingentlich vom Wassermolekül stammt. Wird dieses H-Atom zum Carbonylkohlenstoffatom transportiert, so wird das originale Zuckermolekül wieder gebildet und zugleich kann die Umkehrung der räumlichen Struktur des Zuckermoleküls stattfinden:

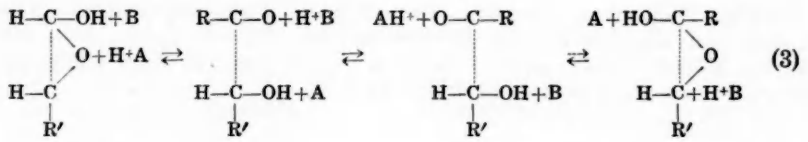


(2)

(iii) Der letzte Mechanismus, der von Lowry[9] stammt und heute im allgemeinen angenommen wird, beruht auf der prototropischen Um-

(7) M. Lowry, *Trans. Chem. Soc.*, **83** (1903), 1314.
(8) E. F. Armstrong, *Trans. Chem. Soc.*, **83** (1903), 1309.
(9) M. Lowry, *J. Chem. Soc.*, **1925**, 1384.

wandlung des Zuckermoleküls, die mit Hilfe der Brönstedschen Säure H^+A und Base B herbeigeführt wird. Das Reaktionsschema ist aus der folgenden Gl. ohne weiteres klar:



(3)

Wäre Reaktion (1) massgebend für die Mutarotation des Zuckers, so müsste, wie darauf schon in Einleitung hingewiesen wurde, ein O-Atom in einem Zuckermolekül zu gleicher Zeit der Mutarotation gegen die des Wassers ausgetauscht werden. Da aber dies nach dem vorliegenden Versuche bei Zimmertemperatur sicherlich nicht der Fall ist, kann Reaktion (1) mindestens bei Zimmertemperatur kein Hauptteil des Mechanismus der Mutarotation sein. Ebenso wenig wahrscheinlich ist Reaktion (2) im Lichte der Versuche, die von Fredenhagen und Bonhoeffer[10] durchgeführt wurde. Von diesen beiden Autoren wurde nämlich festgestellt, dass keine an C gebundenen H-Atome während der Mutarotation der Glucose bei Zimmertemperatur gegen die des Wassers ausgetauscht werden. Wäre aber Reaktion (2) der Hauptteil des Mechanismus der Mutarotation, so müsste offensichtlich ein an C (Carbonylkohlenstoffatom!) gebundenes H-Atom zu gleicher Zeit der räumlichen Umkehrung des Zuckermoleküls durch das des Wassers ersetzt werden.

So bleibt nur noch die letzte Reaktion (3) übrig. Nach diesem Mechanismus brauchen keine H- bzw. O-Atome im Zuckermolekül während seiner räumlichen Umkehrung gegen die des Wassers ausgetauscht werden. Weiter steht dieser Mechanismus mit der wohl bekannten Tatsache im Einklang, dass die Mutarotation des Zuckers eine typische säure-basekatalytische Reaktion ist. Auf diese Weise nehmen wir den letzten Mechanismus (iii) d.h. Reaktion (3) als den wahrscheinlichsten Mechanismus der Mutarotation des Zuckers an. Dabei müssen wir aber darauf aufmerksam machen, dass dieser Schluss nur bei Zimmertemperatur unbeschränkt gültig ist, nicht jedoch bei hohen Temperaturen. Die Nichtaustauschbarkeit der an C gebundenen H-Atome wurde nämlich von Fredenhagen und Bonhoeffer bei Zimmertemperatur bestätigt. Ebenso wird die Nichtaustauschbarkeit der O-Atome bei vorliegendem Versuche nur bei Zimmertemperatur festgestellt. Dagegen fanden wir bei erhöhten Temperaturen (bei 55°C. und 100°C.), dass ein O-Atom des Glucosemoleküls fast ebenso schnell wie die Mutarotation ausgetauscht wird. Dies weist ohne weiteres darauf hin, dass bei hohen Temperaturen die räumliche Struktur des Zuckermoleküls auch durch Reaktion (1) umgekehrt werden kann. So ist durchaus möglich, dass die Mutarotation des Zuckers bei niedrigen Temperaturen fast ausschliesslich nach dem prototropischen Mechanismus stattfindet aber bei erhöhten Temperaturen daneben noch andere Art der Reaktionen eintreten und mindestens ein Teil der Um-

(10) H. Fredenhagen und K. F. Bonhoeffer, *Z. phys. Chem.*, **A181** (1938), 392.

kehrung der räumlichen Struktur des Zuckermoleküls dadurch herbeigeführt wird.

Zum Schluss möchten wir Herrn Prof. Akabori für seine freundlichen Katschläge herzlichst danken. Der Nippon Gakujutu-Sinkôkai (der Japanischen Gesellschaft zur Förderung der Wissenschaft) sowie der Hattori Hôkôkai (der Hattori Stiftung) sind wir für ihre finanzielle Unterstützung zu bestem Dank verpflichtet.

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und chemische Forschung
und
Osaka Teikoku Daigaku
Rigaku-bu
Kagaku Kyositu
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Studies on the Derivatives of 3-Hydroxyflavanone (Dihydroflavonol). I. On the Action of Lead Tetraacetate on Flavanone and 4′-Methoxyflavanone.

By Taichiro OYAMADA.

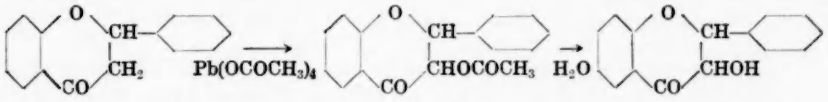
(Received July 28, 1941.)

Several years ago, fustin[1], isolated from *Rhus succedanea* L., was confirmed by the present author to be a derivative of 3-hydroxyflavanone (dihydroflavonol), namely 3,7,3′,4′-tetrahydroxyflavanone. Since then two new derivatives of this group, alpinon[2] and ampeloptin[3], have been isolated from plants by Japanese workers. Consequently, it is possible that many other new derivatives of this series may occur in nature. It would, therefore, be of great interest to synthesise many compounds of this new class and to investigate the behaviour of these compounds.

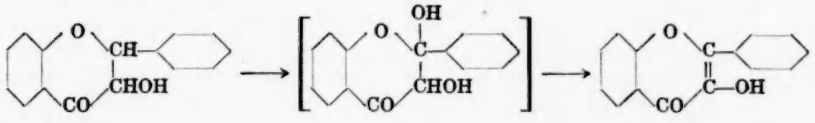
By the systematic studies of Criegee and others[4], it has been shown that lead tetraacetate is an important reagent for the oxidative fission of α-glycols. However, only a few researches[5] have been carried out as

(1) *J. Chem. Soc. Japan*, **55** (1935), 755–790; *Ann.*, **538** (1939), 44.
(2) Y. Kimura, *J. Pharm. Soc. Japan*, **57** (1937), 147.
(3) T. Kubota, *J. Chem. Soc. Japan*, **59** (1938), 1153.
(4) R. Criegee, *Ber.*, **64** (1931), 260; *Ann.*, **507** (1933), 159; *Ber.*, **68** (1935), 665 etc.
(5) R. C. Morris, W. E. Hanfold and R. Adams, *J. Am. Chem. Soc.*, **57** (1935), 951; W. Hückel and K. Hartmann, *Ber.*, **70** (1937), 961; O. Dimroth and R. Schweizer, *Ber.*, **56** (1923), 1375; T. Reichstein and C. Montigel, *Helv. Chim. Acta*, **22** (1939), 1212 etc.

to the use of this reagent in substitution. The present author attempted to synthesise the derivatives of 3-hydroxyflavanone, in replacing the active hydrogen (position 3) in flavanones with an acetoxy-group by lead tetra-acetate and the subsequent hydrolysis of the resulting esters, as shown in the following scheme:



The solution of flavanone (1 mol.) and lead tetraacetate (1 mol.) in glacial acetic acid was heated at 80–90°, until all unchanged tetraacetate disappeared, which was indicated by the absence of the formation of the brown colloidal lead peroxide on dilution of the solution with water. As the product thus obtained was viscous and difficult to purify, it was directly subjected to hydrolysis. The crude product was heated on the water-bath for a short time with alcohol containing concentrated hydrochloric acid and, on cooling, a colourless leaf-like crystalline compound, melting indefinitely at 140–175°, separated out. Even after several crystallisations from alcohol, the substance was still impure and melted indefinitely at 170–178°. However, it could be purified by converting it into the pure crystalline acetate by treatment with acetic anhydride and a drop of concentrated sulphuric acid, and then by hydrolysing it in an acidic medium in a current of carbon dioxide in order to prevent it from being oxidised. The compound thus purified melted at 183–184° and was very sensitive to oxygen, especially in the presence of alkali. It was partly soluble in hot alkali with the formation of a yellow solution. On acidifying the alkaline solution, a compound, melting at 170°, separated, which was proved to be flavonol by the method of the mixed melting point. For the explanation of the mechanism of this reaction, attention was directed to the fact that 7,3′,4′-trimethoxy-3-hydroxyflavanone (trimethylfustin) yielded 7,3′,4′-trimethoxy-3-hydroxyflavone (trimethylfisetin) when treated with alkali[6]. The formation of flavonol is obviously due to the oxidation of 3-hydroxyflavanone (dihydroflavonol), as probably indicated in the following scheme:



On the other hand, the present author tried to purify the hydrolysed product by the chromatographic method, using magnesia as an adsorbent, and observed that most of the product was adsorbed by magnesia, which became yellow, and that the substance adsorbed was regenerated as flavonol on dissolving the adsorbent in hydrochloric acid. This phenomenon was also observed in the pure compound, melting at 183–184°, and, moreover, in 4′-methoxy-3-hydroxyflavanone (4′-methoxydihydroflavonol)

(6) *J. Chem. Soc. Japan*, **55** (1935), 763 and 786; *Ann.*, **538** (1939), 46 and 51.

and trimethylfustin (trimethyldihydrofisetin). It is noteworthy that the derivatives of 3-hydroxyflavanone showed an extreme facility in forming the corresponding flavonols when they were adsorbed by magnesia or a similar weak basic substance. Furthermore, the author conducted the chromatographic adsorption in a current of hydrogen in order to avoid oxidation, but he could not obtain a good result, owing to the difficulty of securing the complete exclusion of oxygen during the whole operation.

From the part unadsorbed by magnesia, a new compound, melting at 132–133°, was obtained in a small quantity. This compound was very stable and did not change on heating at a comparatively high temperature with mineral acid in a sealed tube. Further study of this compound is now in progress.

The similar treatment was applied to 4'-methoxyflavanone with a view to synthesise 4'-methoxy-3-hydroxyflavanone. After a number of experiments, the expected compound was obtained together with a small quantity of an unknown compound, melting at 118–119°, by the procedure described in the experimental part. As the author had previously prepared the same compound in another way[7], the compound obtained here was easily proved to be the expected one by direct comparison. The compound was also converted into the corresponding flavonol by adsorption with magnesia.

This investigation, both in the synthetic and the natural derivatives of flavanone, is now being extended at this laboratory.

Experimental. *Preparation of Lead Tetraacetate.* Lead tetraacetate was prepared according to the Dimroth method modified by Gattermann[8]. Red lead oxide (minium) (120 g.) was gradually added to glacial acetic acid (450 c.c.), containing acetic anhydride (12 c.c.), and thoroughly stirred while it was kept at 60–65°. Considerable amount of lead tetraacetate was deposited on cooling. On recrystallising from glacial acetic acid, it was obtained as colourless crystals. Although it is very unstable in the dry state, it can be kept for a long time by covering it with glacial acetic acid.

Action of Lead Tetraacetate on Flavanone. A solution of 24 g. of flavanone and 48 g. of lead tetraacetate in 400 c.c. of glacial acetic acid was heated in the water-bath at 80–90° for two hours. The completion of the reaction was proved by the absence of formation of brown colloidal lead peroxide on dilution of the solution with water. The solution was poured into water and extracted with ether. The ethereal extract was washed with water and then with sodium bicarbonate solution in order to remove acetic acid, dried over anhydrous sodium sulphate and evaporated. The residual oil was then distilled under a reduced pressure of 3 mm., and a viscous liquid, boiling at 198–200°, was obtained. The yield was 22 g. The viscous liquid was ascertained to be a mixture by further experiment.

Hydrolysis. The liquid thus obtained (13 g.) was heated with alcohol (150 c.c.) containing concentrated hydrochloric acid (30 c.c.) on the

(7) *J. Chem. Soc. Japan*, **56** (1936), 980.
(8) L. Gattermann, "Die Praxis des organischen Chemikers," (1936), 123.

water-bath for thirty minutes. On cooling, a leaf-like crystalline compound (6.2 g.), melting at 140–175°, was deposited. After several crystallisations from alcohol, it separated in crystals, sintering at 170° and melting completely at 178°. Although the purification by means of several recrystallisations from alcohol and other solvents was attempted, the substance remained impure and melted indefinitely. Therefore, the purification by recrystallisation was discarded and an adsorption method was then tried, but without success. Finally, it could be purified through its pure acetate in the way described in the following experiments.

Preparation of 3-Acetoxyflavanone. The acetylation of the hydrolysed product (4 g.), was effected by the action of acetic anhydride (20 g.) and a drop of concentrated sulphuric acid at room temperature. The acetylated product was poured into water, when an oil separated, and solidified on standing. After several crystallisations from alcohol, 3-acetoxyflavanone melted at 94–94.5°. The yield was 2.3 g. Found: C, 72.60; H, 5.21. Calc. for $C_{17}H_{14}O_4$: C, 72.34; H, 4.96%.

Preparation of 3-Hydroxyflavanone. The above acetate (2 g.) was heated with alcohol (40 c.c.), containing concentrated hydrochloric acid (20 c.c.), on the water-bath for an hour in a current of carbon dioxide. On cooling, a leaf-like crystalline compound separated out. After recrystallisation from alcohol, in an atmosphere of carbon dioxide in order to avoid the contact with oxygen, 3-hydroxyflavanone separated in crystals, melting at 183–184° when heated rapidly in the bath which had been previously heated to about 175°. However, it began to melt at lower temperature when heated from low temperature. The yield was 0.8 g. It is insoluble in cold alkali, but soluble in hot alkali with the formation of a yellow solution. On acidifying this alkaline solution, flavonol, melting at 170°, separated out. The 3-hydroxyflavanone was adsorbed by magnesia, which became yellow, and, on dissolving the magnesia in hydrochloric acid, flavonol was recovered. Further study of the 3-hydroxyflavanone is now in progress. Murakami and Irie[9] had prepared the same compound by the action of hydrogen peroxide on 2′-hydroxychalkone in the presence of alkali and reported its melting point as 174–177°. Found: C, 75.28; H, 5.42. Calc. for $C_{15}H_{12}O_3$: C, 75.00; H, 5.00%.

Chromatographic Adsorption of the Hydrolysed Product. With the object of purifying the hydrolysed product, a chromatographic adsorption was tried, using magnesia as an adsorbent. When the colourless solution of the hydrolysed product (0.5 g.) in benzene (100 c.c.) was passed through the Tswett column, modified by Winterstein (22 cm. in height) and which was filled with magnesia (37 g.), the upper layer (3/4) of the magnesia became yellow, indicating an adsorption. On dissolving the yellow part of the magnesia in hydrochloric acid, a yellowish compound separated. It was collected and recrystallised from alcohol, when it separated in yellowish crystals, melting at 170°. No depression of the melting point was caused by admixture with an authentic specimen of flavonol. The yield was 0.3 g. The solution passed through magnesia was evaporated and a needle-like crystalline compound, melting at 132–133°, was obtained on recrystallising from alcohol. The yield was 0.08 g.

(9) M. Murakami and T. Irie, *Proc. Imp. Acad.* (Tokyo), **11** (1935), 229.

No change was observed on heating this substance with a 20% alcoholic solution of hydrochloric acid in a sealed tube. Further study of this compound is now being carried out.

Hydrolysis of the Product formed in the Action of Lead Tetraacetate on Flavanone by means of Methyl-alcoholic Soda. The reaction product (2 g.) was dissolved in a 2.5% methyl-alcoholic soda (50 c.c.) and the solution was allowed to stand at room temperature for five days, when a dark yellow crystalline compound was deposited. On recrystallising it from alcohol, containing a small quantity of hydrochloric acid, a yellow compound, melting at 170°, was obtained and identified as flavonol by the method of the mixed melting point. The yield was 0.8 g.

Action of Lead Tetraacetate on 4′-Methoxyflavanone. A solution of 4′-methoxyflavanone (4 g.) and lead tetraacetate (7 g.) in glacial acetic acid (100 c.c.) was heated in the water-bath at 80–90° for two hours. After the removal of lead compound by the saturation with hydrogen sulphide, most of the acetic acid was distilled off under the reduced pressure, and the residue was poured into water and extracted with ether. The ethereal extract was washed with water, dried over anhydrous sodium sulphate and evaporated. On standing, the residue partly crystallised. The crystals were collected and recrystallised from ether, from which they separated in colourless crystals, melting at 118–119°. The yield was 0.7 g. Further study of this compound is now in progress.

The viscous filtrate from the above-mentioned crystalline compound was subjected to hydrolysis. The viscous liquid (3 g.) was heated with alcohol (40 c.c.), containing concentrated hydrochloric acid (4 g.) and water (2 c.c.), on a water-bath for an hour and, on cooling, a crystalline compound, melting at 143–153°, separated. This compound was purified by several crystallisations from alcohol and then from benzene. The compound thus purified melted at 172–174°. The yield was 0.5 g. This compound was proved to be identical with the 4′-methoxy-3-hydroxyflavanone, which had been previously prepared in another way by the present author. It was also converted into 4′-methoxy-3-hydroxyflavone (4′-methoxyflavonol), melting at 230–231°, by adsorption with magnesia.

In conclusion, the author wishes to express his sincere thanks to Mr. Shigemi Oba, the Director of the Yonezawa Higher Technical School, and to Prof. Tosaziro Yoshida of this school for their encouragements throughout this work. He also expresses his hearty thanks to the Department of Education for the Scientific Research Expenditure which has defrayed most of the cost of this research.

Yonezawa Higher Technical School,
Yonezawa.

Synthesis of *p*-Isopropyl-*α*-methylhydrocinnamic aldehyde.

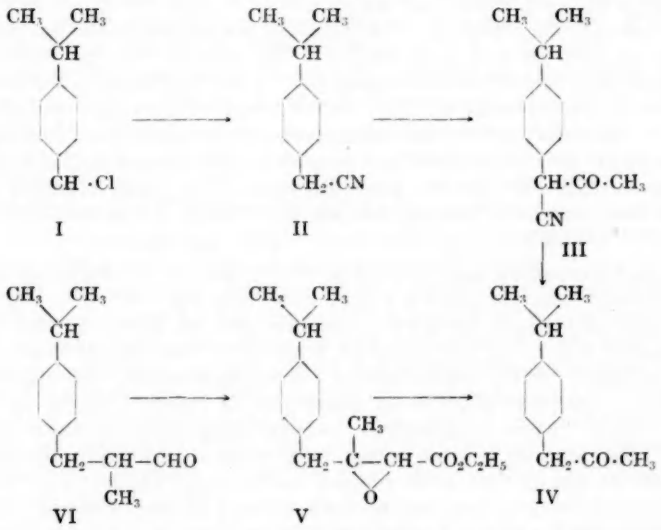
By Masataro YAMASHITA and Tokiyoshi MATSUMURA.

(Received July 28, 1941.)

Knorr and Weissenborn[1] synthesised *p*-isopropyl-*α*-methylhydrocinnamic aldehyde by condensing cuminaldehyde with propionaldehyde in the presence of alcoholic potash and then reducing the product with hydrogen, using nickel as a catalyser. Since then this compound has been used as perfume. More recently, the compound has been synthesised in the Société des Usines Chimiques[2] by heating calcium *p*-isopropyl-*α*-methylhydrocinnamate with calcium formate or by heating *p*-isopropyl-*α*-methylhydrocinnamic acid with formic acid in the presence of metallic oxides, such as oxide of Ti, Mn, Al, Zn or Th. For this synthesis, *p*-isopropyl-*α*-methylhydrocinnamic acid was first synthesised by the condensation of cuminyl chloride with ethyl methylmalonate in the presence of sodium ethoxide and subsequent decomposition of the free acid liberated from the ester.

Two new methods, both starting from cuminyl chloride, of synthesising *p*-isopropyl-*α*-methylhydrocinnamic aldehyde have been devised by the present authors.

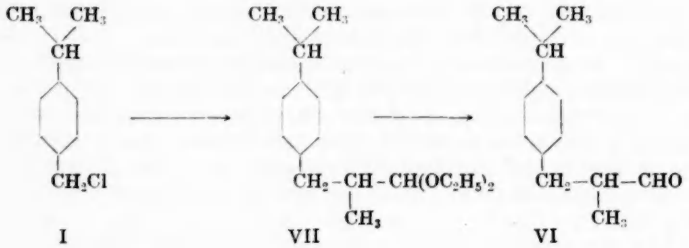
The first method. Cuminyl chloride (I) was first converted into *p*-isopropylbenzyl cyanide (II). The cyanide and ethyl acetate were condensed in the presence of sodium ethoxide to form *α*-*p*-isopropylphenyl-



(1) A. Knorr and A. Weissenborn (Winthrop Chemical Co., Inc.), A.P. 1844013 (1932).
(2) F.P. 833644 (1938).

acetoacetonitrile (III), which was converted into *p*-isopropylbenzyl methyl ketone (IV). The ketone and ethyl monochloroacetate were again condensed to yield ethyl *α,β*-epoxy-*γ*-*p*-isopropylphenyl-*β*-methylbutyrate (V), which, on saponification, gave the desired *p*-isopropyl-*α*-methylhydrocinnamic aldehyde (VI) as shown in the accompanying scheme.

The second method. Cuminyl chloride (I) was converted by the condensation with the diethylacetal of *α*-bromopropionaldehyde into the diethylacetal of *p*-isopropyl-*α*-methylhydrocinnamic aldehyde (VII). The acetal, on hydrolysis with dilute hydrochloric acid, yielded the desired *p*-isopropyl-*α*-methylhydrocinnamic aldehyde (VI), as shown in the following scheme:



I VII VI

Experimental. p-*Isopropylbenzyl Cyanide* (II). This compound was synthesised by Rossi[3] and by Komppa[4] by heating cuminyl chloride with potassium cyanide in a sealed tube. However, the present authors were able to prepare it with an 85% yield in the following way: Cuminyl chloride (170 g.) and alcohol (170 g.) were added to a solution of potassium cyanide (65 g.) in water (60 c.c.), and the mixture was boiled for 3 hours. On cooling, it separated potassium chloride, which was filtered off and washed with alcohol. The filtrate and the washings were combined and the alcohol evaporated. The residue was extracted with ether and the ethereal extract was washed with water and dried over calcium chloride. After the ether was evaporated, the residual oil was subjected to fractional distillation under reduced pressure, when an oil boiling at 125–128°/9 mm. passed over. The yield was 85% of the theoretical. The oil has n_D^{25} 1.5078, d_4^{25} 0.9619, $[R_L]_D$ 49.28 (Calc. for $C_{11}H_{13}N$: 49.22).

α-p-*Isopropylphenylacetoacetonitrile* (III). A mixture of *p*-isopropylbenzyl cyanide (318 g.) and ethyl acetate (264 g.) was added to a solution of sodium (60 g.) in absolute alcohol (700 c.c.) and the whole was heated to boiling for about an hour on a water-bath, until it became a pasty mass. After being heated for an hour more, the mass solidified completely and was allowed to stand for 12 hours. Water (3 kg.) was then added, when unchanged *p*-isopropylbenzyl cyanide separated, which was removed by extraction with ether. The aqueous residue was acidified at about 10° with glacial acetic acid (100 c.c.). The yellow oil, thus obtained was extracted with ether and the ethereal extract was

(3) A. Rossi, *Ann., Suppl.*, **1** (1861), 139.
(4) G. Komppa, *Ber.*, **68** (1935), 1269.

washed successively with an aqueous solution of sodium carbonate and with water. After the ethereal extract was dried over calcium chloride, the ether was evaporated, and the residual oil solidified. The yield was 290 g. (72% of the theoretical). Although it was pure enough for the next preparation, it was recrystallised from methyl alcohol, from which it separated in colourless needles melting at 84–85°. Found: N, 7.26. Calc. for $C_{13}H_{15}ON$: N, 6.96%.

The semicarbazone crystallised from alcohol in colourless aggregated crystals melting at 156°. Found: N, 21.82. Calc. for $C_{18}H_{18}ON_4$: N, 21.70%.

p-*Isopropylbenzyl Methyl Ketone* (IV).—This compound has already been prepared by Bradfield, Pritchard and Simonsen[5] by condensing cuminaldehyde with ethyl α-bromopropionate in the presence of sodium ethoxide, and then hydrolysing the condensation product, namely ethyl α,β-epoxy-β-cuminyl-β-methylpropionate, with methyl alcoholic potassium hydroxide.

The present authors synthesised this compound in the following way: Powdered α-*p*-isopropylphenylacetoacetonitrile (120 g.) was added, with constant stirring, to concentrated sulphuric acid (170 c.c.), cooled at −10°. After all the nitrile was added, the mixture was warmed to 60° and a brown solution was obtained. After this was cooled to 0°, water (850 c.c.) was rapidly added and the whole was again heated, with constant stirring, for two hours on a water-bath. The green solution thus obtained was cooled, and the supernatant oil was separated. The aqueous solution was extracted several times with ether. The oil and ethereal extracts were combined, washed with water, dried over anhydrous sodium sulphate and evaporated. The residual oil was purified by distillation under diminished pressure, and a fraction, boiling at 125–128°/16 mm., was collected. This fraction has n_D^{28} 1.5033, d_4^{28} 0.9538, $[R_L]_D$ 54.33 (Calc. for $C_{12}H_{16}O$: 54.03).

The semicarbazone crystallised from alcohol in colourless prisms melting at 142–143°. Found: N, 18.20. Calc. for $C_{13}H_{19}ON$: N, 18.03%.

*Ethyl α,β-Epoxy-γ-*p*-isopropylphenyl-β-methylbutyrate* (V). Absolute alcohol (55 g.) was added to pieces of sodium (13.8 g.) covered with dry benzene (200 g.). After all the sodium dissolved, the solution was maintained at 0°, and, to this, *p*-isopropylbenzyl methyl ketone (88 g.) and ethyl monochloroacetate (62 g.) were added and stirred for two hours at 0°. The mixture was allowed to stand for 40 hours at the ordinary temperature, poured into ice-cold water (500 g.) and acidified with glacial acetic acid (5 c.c.). The supernatant oily layer was separated and the lower aqueous layer was extracted with benzene. The oil and benzene solution were combined, washed with water, dried over anhydrous sodium sulphate and evaporated. The residual oil was subjected to fractional distillation under reduced pressure of 11 mm., and a fraction distilling at 164–167°, was collected. The yield was 76 g. (58% of the theoretical). Found: C, 73.05; H, 8.62. Calc. for $C_{16}H_{22}O_3$: C, 73.23; H, 8.46%. It has n_D^{28} 1.4987 and d_4^{28} 1.0308.

p-*Isopropyl-α-methylhydrocinnamic Aldehyde* (VI). Ethyl α,β-epoxy-

(5) A. E. Bradfield, R. R. Pritchard and J. L. Simonsen, *J. Chem. Soc.*, **1937**, 760.

γ-*p*-isopropylphenyl-β-methylbutyrate (60 g.) was stirred for two hours at 35° with a 10% solution of sodium hydroxide (100 g.), and a lustrous paste was obtained. After this was mixed with a 10% solution of oxalic acid (110 g.), the mixture was distilled in steam. The oil passed over with vigorous effervescence and was extracted with ether. The ethereal extract was dried over anhydrous sodium sulphate and evaporated. The residual oil was distilled under reduced pressure of 10 mm. in a current of carbon dioxide, and a fraction, boiling at 128–131°, was collected. The oil has n_D^{28} 1.5030, d_4^{28} 0.9529, $[R_L]_D$ 58.99 (Calc. for $C_{13}H_{16}C\overline{=}_3$: 58.64).

The semicarbazone crystallised from alcohol in glazed colourless plates melting at 169–170°. Found: N, 16.24. Calc. for $C_{15}H_{21}ON_2$: N, 16.21%.

Diethylacetal of p-*Isopropyl-α-methylhydrocinnamic Aldehyde* (VII). A mixture of cuminyl chloride (115 g.) and diethylacetal of α-bromopropionaldehyde (140 g.) was gradually added, with constant stirring, to sodium (35 g.), cut into pieces and covered with ether. The stirring was continued, while the temperature rose gradually to boiling. The mixture was cooled with water and allowed to stand for five hours. After the reaction had subsided, the mixture was heated for 6 hours on a water-bath with a reflux condenser. The reaction product was then cooled and the oily part was removed by decantation. The residue left behind in the vessel was extracted with ether. The oily part and ethereal extract were combined, washed with water, dried over anhydrous sodium sulphate and evaporated. The residual oil was distilled under reduced pressure of 13 mm., and a fraction, boiling at 117–122°, was collected. Found: C, 77.01; H, 10.80; Calc. for $C_{17}H_{28}O_2$: C, 72.22; H, 10.92%.

It has n_D^{25} 1.4850, d_4^{25} 0.9376, $[R_L]_D$ 80.69 (Calc. for $C_{17}H_{28}O_2\overline{=}_3$: 80.39).

The Conversion of the Acetal into p-*Isopropyl-α-methylhydrocinnamic Aldehyde*. The acetal (60 g.) was heated with a 3% solution of hydrochloric acid (600 c.c.) for fifty minutes under a reflux condenser. After the mixture was cooled, the supernatant oily layer was extracted with ether. The ethereal extract was washed with an aqueous solution of sodium carbonate and then with water. The extract was dried over anhydrous sodium sulphate and evaporated. The residual oil was subjected to fractional distillation under reduced pressure of 12 mm. in a current of carbon dioxide, when a colourless oil boiling at 133–135° passed over. The yield was 33 g. (77% of the theoretical). The melting point of the semicarbazone was not depressed by admixture with the specimen synthesised by the first method.

In conclusion, the authors wish to express their hearty thanks to Professor Eiichi Funakubo, Osaka Imperial University, for the assistance in the microanalyses of nitrogen of the substances described above.

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Austauschreaktion der Wasserstoffatome im festen Anilinchlorhydrat und seine Derivate. II. *p*-Toluidinchlorhydrat (Auszug).[1]

Von **Jisaku KURODA** und **Nobukazu OKAZAKI.**

(Eingegangen am 8. September 1941.)

Inhaltsübersicht. Wird das in die Ammoniumgruppe D eingeführte *p*-Toluidinchlorhydrat unterhalb bzw. oberhalb seines Schmelzpunktes erwärmt, so tauschen die in die Ammoniumgruppe eingeführten D-Atome ihre Plätze gegen die der im Benzolkern befindlichen Kernwasserstoffatome aus. Die Anzahl der sich an dieser Austauschreaktion beteiligenden Kernwasserstoffatome ergibt unterhalb des Schmelzpunktes d.h. bei der Reaktion, die in der mit blossem Auge fest aussehenden Phase stattfindet, nur zwei. Dagegen wächst sie plötzlich bis auf vier an, so bald als die Erwärmungstemperatur den Schmelzpunkt überschreitet und das *p*-Toluidinchlorhydrat schmilzt. Dies deutet ohne weiteres darauf hin, dass der Mechanismus der Reaktion, die unterhalb des Schmelzpunktes in der festen Phase vor sich geht, ein ganz anderer ist als bei der Reaktion in der geschmolzenen Phase. Es liegt also die Annahme nahe, dass die erstere Reaktion wirklich in der echten festen Phase stattfindet und die Anzahl sowie die Lage der sich an der Reaktion beteiligenden Kernwasserstoffatome mit der geometrischen Ordnung des Kristallgitters in engem Zusammenhang steht.

Einleitung. Erwärmt man das in die Ammoniumgruppe D eingeführte Anilinchlorhydrat unterhalb bzw. oberhalb seines Schmelzpunktes, so tauschen diese D-Atome ihre Plätze gegen die H-Atome aus, die im Benzolkern befindlich sind. Diese von Harada und Titani[2] gefundene eigenartige Platzwechselreaktion der H-Atome des Anilinchlorhydrats wurde von einem von uns und Koizumi[3] eingehend untersucht. Dabei kamen wir zu dem Schluss, dass die oberhalb des Schmelzpunktes beobachtete Reaktion zweifellos in der flüssigen Phase vor sich geht. Aber über den Mechanismus der Reaktion, die unterhalb des Schmelzpunktes in der mit blossem Auge fest aussehenden Phase stattfindet, konnten wir bloss aus dem damals erhaltenen Versuchsergebnis keinen sicheren Schluss ziehen, ob es sich wirklich um die Reaktion in der echten festen Phase handelt oder die Reaktion hauptsächlich in der hochdispersen flüssigen Phase stattfindet, die unter dem Einfluss der Verunreinigungen insbesondere an den Kanten bzw. Ecken der Kriställchen entstehen.

Wäre die letztere Reaktion massgebend, so müsste die Anzahl der Kernwasserstoffatome, die sich an der Reaktion beteiligen, immer dieselbe Grösse besitzen, ohne Unterschied ob man die Reaktion unterhalb oder oberhalb des Schmelzpunktes untersucht, weil in diesem Fall der massgebende Mechanismus der Reaktion immer derselbe sein soll. Falls

(1) N. Okazaki und J. Kuroda, *J. Chem. Soc. Japan*, **62** (1941), 57. I. Mittl.: dies Bulletin, **16** (1941), 371.

(2) M. Harada und T. Titani, dies Bulletin, **11** (1936), 554.

(3) N. Okazaki und M. Koizumi, dies Bulletin, **16** (1941), 371.

dagegen die Reaktion oberhalb des Schmelzpunktes hauptsächlich in der flüssigen Phase vor sich geht während sie unterhalb desselben wirklich in der echten festen Phase stattfindet, ergibt sich die Möglichkeit, dass die oben angegebene Anzahl einen ganz verschiedenen Wert besitzt, je nachdem ob man die Reaktion oberhalb bzw. unterhalb des Schmelzpunktes untersucht. Die vorliegenden Versuche, die unter Verwendung des *p*-Toluidinchlorhydrats ausgeführt wurden, ergaben, dass dies wirklich der Fall ist; die Anzahl der Kernwasserstoffatome des *p*-Toluidinchlorhydrats, die sich an der Reaktion unterhalb des Schmelzpunktes beteiligen, ergibt zwei, während sie plötzlich bis auf vier anwächst, sobald als die Erwärmungstemperatur den Schmelzpunkt überschreitet und das *p*-Toluidinchlorhydrat schmilzt. Dies beweist ohne weiteres, dass der Mechanismus der Reaktion, die unterhalb des Schmelzpunktes in der mit blossem Auge fest aussehenden Phase stattfindet, ganz anders angenommen werden muss als die Reaktion, die oberhalb des Schmelzpunktes in der geschmolzenen Phase stattfindet.

Versuchsmethode und -ergebnisse. Die Versuchsmethode ist genau dieselbe wie die in der letzten Mitteilung beim Versuch mit dem Anilinchlorhydrat benutzt wurde.

Das *p*-Toluidinchlorhydrat wird durch die Vereinigung des reinen *p*-Toluidins mit der reinen Salzsäure hergestellt. Das so hergestellte *p*-Toluidinchlorhydrat wird dann durch die zweimalige Umkristallisation aus Alkohol sowie durch die zweimalige Fällung aus alkoholischer Lösung durch Äther gereinigt. Es schmilzt bei 242° bis 243.5°.

Die Versuchsergebnisse sind in Tabelle 1 zusammengestellt, wo die Versuchsnr. die zeitliche Reihenfolge der einzelnen Versuche zeigt und das Austauschäquivalent *nk* auf genau dieselbe Weise wie beim Anilinchlorhydrat mit Hilfe des D-Gehaltes des schweren Wassers ermittelt wird (vgl. Gl. (1) in I. Mitt.), das sich mit dem nicht erwärmten sowie erwärmten *p*-Toluidinchlorhydrat im Austauschgleichgewicht befindet. Die Bezeichnung „P_2O_5" und „Sublimation" in der zweiten letzten Spalte der Tabelle bedeutet, dass das *p*-Toluidinchlorhydrat vor der Erwärmung resp. über Phosphorpentoxyd bzw. durch die Sublimation im Hochvakuum getrocknet wurde.

Dass das *p*-Toluidinchlorhydrat auch nach der längeren Erwärmung auf hohen Temperaturen nicht so merklich zersetzt wurde, wird aus Tabelle 2 ohne weiteres ersichtlich, wo der Schmelzpunkt sowie die äussere Beschaffenheit einiger Proben des *p*-Toluidinchlorhydrats nach der Beendigung der Versuche wiedergegeben ist (vgl. Tabelle 1).

Zeichnet man die in Tabelle 1 angegebenen Daten graphisch ein, so erhält man Abb. 1, wo die Nummer bei jedem kleinen Kreis die Erwärmungsdauer angibt. Diese Abb. 1 zeigt, dass das Austauschäquivalent *nk*, das in erster Annäherung die statistische Anzahl *n* der Kernwasserstoffatome angibt, die sich an der Platzwechselreaktion beteiligen, mit steigender Temperatur (und bei konstant gehaltener Erwärmungsdauer) allmählich anwächst. Aber es wächst nur bis zu etwa zwei, so lange als die Erwärmungstemperatur unterhalb des Schmelzpunktes bleibt. Überschreitet dagegen die Erwärmungstemperatur den Schmelzpunkt, so wächst der Gleichgewichtswert von *nk* plötzlich bis auf etwa vier.

Tabelle 1. Die Austauschreaktion des *p*-Toluidinchlorhydrats in fester und geschmolzener Phase.

Versuchsnr.	Erwärmungs-temp. °C.	Erwärmungs-dauer in Stdn.	*nk*	Trocknung	Bemerkung
1-4	ohne Erwärmung		±0.2	P_2O_5	fest
24	110	3.5	0.0	P_2O_5	,,
25	140	3.5	0.1	P_2O_5	,,
26	170	3.5	0.2	P_2O_5	,,
27	184	3.5	0.6	P_2O_5	,,
28	200	3.5	0.8	P_2O_5	,,
29	200	4	1.5	P_2O_5	,,
30	217	3.5	1.8	P_2O_5	,,
22	220	7	2.1	Sublimation	,,
20	220	14	2.2	Sublimation	,,
18	220-222	45	1.9	Sublimation	,,
10	222-223	23	2.1	P_2O_5	,,
23	223.5	1	1.9	Sublimation	,,
21	223.5	3.5	2.1	Sublimation	,,
5	233-235	2	1.5	P_2O_5	,,
6	233-235	5	2.1	P_2O_5	,,
7	233-235	20	2.1	P_2O_5	,,
8,9	233-235	50	2.1	P_2O_5	,,
31	235	3.5	1.7	P_2O_5	,,
10	238-240	20	2.3	P_2O_5	wenig zusammen-gesintert
32	243	3.5	3.1	P_2O_5	Schmelzpkt.
11	246-249	2	2.6	P_2O_5	flüssig
12	246-249	5	3.2	P_2O_5	,,
13	246-249	20	4.2	P_2O_5	,,
14	246-249	50	4.5	P_2O_5	,,
33	248	1/6	2.0	P_2O_5	,,
15	249	15	4.2	Sublimation	,,
17	250	7	4.5	Sublimation	,,
16	250	10	4.4	Sublimation	,,

Tabelle 2. Schmelzpunkt und äussere Beschaffenheit des *p*-Toluidinchlorhydrats nach der Beendigung der Versuche.

Versuchsnr.	Erwärmungs-temp. °C.	Erwärmungs-dauer in Stdn.	Schmelzpunkt nach dem Versuch	äussere Beschaffenheit nach dem Versuch
—	onhe Erwärmung		242-243.5°	farblos
14	246-249	50	—	braun gefärbt und ganz schwach nach Chinon gerochen
15	249	15	240-243° (von 232° ab zusammenge-sintert)	hell bräunlich gefärbt
16	250	10	239.5-241.5°	fast keine Färbung
17	250	7	239.5-242.5°	hell bräunlich gefärbt

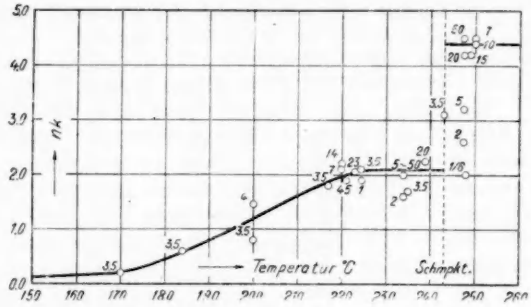

Abb. 1. Das Austauschäquivalent *nk* des *p*-Toluidinchlorhydrats in Abhängigkeit von der Erwärmungsdauer und -temperatur.

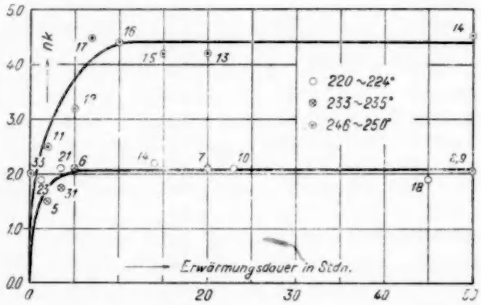

Abb. 2. Das Austauschäquivalent *nk* des *p*-Toluidinchlorhydrats in Abhängigkeit von der Erwärmungsdauer unterhalb bzw. oberhalb des Schmelzpunktes.

Diese sprungweise Zunahme des Gleichgewichtswertes von *nk* beim Schmelzpunkt kann weiter aus Abb. 2 deutlich ersehen werden, wo der Wert von *nk*, der dicht unterhalb (bei 220–224° sowie 233–235°) sowie oberhalb (bei 246–250°) des Schmelzpunktes beobachtet wird, beide in Abhängigkeit von der Erwärmungsdauer eingetragen ist. Obwohl der Wert von *nk* bei den Temperaturen, die unterhalb des Schmelzpunktes liegen, sogar nach 50 stündiger Erwärmung nur asymptotisch bis zu 2.1 anwächst, wächst er oberhalb des Schmelzpunktes schon nach einigen Stunden Erwärmung bis auf 4.4 an. Dies deutet ohne weiteres darauf hin, dass die Anzahl der Kernwasserstoffatome, die ihre Plätze unterhalb des Schmelzpunktes gegen die in der Ammoniumgruppe befindlichen H-Atome wechseln, nur zwei beträgt, während oberhalb des Schmelzpunktes alle vier H-Atome im Benzolkern sich an der Reaktion beteiligen.

Beim letzten Versuch mit dem Anilinchlorhydrat wird festgestellt, dass die drei in *o*-, *o'*- und *p*-Stellung befindlichen Kernwasserstoffatome ihre Plätze gegen die H-Atome in der Aminogruppe wechseln. Deshalb liegt die Annahme nahe, dass beim vorliegenden Versuch mit dem *p*-

Toluidinchlorhydrat die zwei Kernwasserstoffatome, die ihre Plätze zuerst d.h. schon unterhalb des Schmelzpunktes gegen die H-Atome in der Aminogruppe wechseln, die dieser Gruppe gegenüber in *o*- und *o'*-Stellung befindlichen beiden H-Atome sind. Sobald aber als das *p*-Toluidinchlorhydrat schmilzt, kommen dazu noch die anderen beiden d.h. in *m*- und *m'*-Stellung befindlichen nicht substituierten Kernwasserstoffatome ins Spiel, die unter dem Einfluss der in *p*-Stellung eingeführten Methylgruppe im Vergleich mit dem unsubstituierten Anilinchlorhydrat reaktionsfähiger werden.

Diskussion der Ergebnisse. Über den Mechanismus der vorliegenden Platzwechselreaktion der H-Atome gibt es, wie darauf schon in I. Mittl. hingewiesen wurde, zwei Möglichkeiten: entweder (1), dass die Reaktion nicht nur oberhalb sondern auch unterhalb des Schmelzpunktes immer in einer flüssigen Phase stattfindet, die unterhalb des Schmelzpunktes unter dem Einfluss der Verunreinigungen in hoch disperser Form gebildet wird, oder (2), dass die oberhalb des Schmelzpunktes beobachtete Reaktion in der flüssigen, während die unterhalb des Schmelzpunktes verlaufende Reaktion wirklich in der echten festen Phase stattfindet. Zwischen diesen beiden Möglichkeiten konnten wir aber beim letzten Versuch mit dem Anilinchlorhydrat keine eindeutige Entscheidung treffen, obwohl die letztere Möglichkeit wahrscheinlicher ist als die erstere.

Da aber beim vorliegenden Versuch festgestellt wurde, dass die Anzahl der Kernwasserstoffatome des *p*-Toluidinchlorhydrats, die sich an der Reaktion unterhalb des Schmelzpunktes beteiligen, einen ganz anderen Wert besitzt als oberhalb des Schmelzpunktes, darf wohl geschlossen werden, dass auch der Mechanismus der Reaktion in den beiden Fällen d.h. unterhalb und oberhalb des Schmelzpunktes voneinander ganz anders sein muss; die Reaktion, die unterhalb des Schmelzpunktes beobachtet wird, findet wirklich in der echten festen Phase statt, während die andere oberhalb desselben in der flüssigen Phase verläuft. Beim ersteren Fall können wir den Reaktionsmechanismus etwa so annehmen, dass die Kernwasserstoffatome durch die immer heftiger werdende thermische Schwingung so weit gelockert sind, bis schliesslich ihre Plätze gegen die ebenfalls gelockerten H-Atome in der Aminogruppe des eigenen bzw. der benachbarten Moleküle ausgetauscht werden. Dabei ist durchaus möglich, dass der intermolekulare Austausch der H-Atome durch die zugleich heftig werdende thermische Schwingung der einzelnen Moleküle bei weitem erleichtert wird. Für die Annahme, dass zu dieser Austauschreaktion nicht nur die Kernwasserstoffatome sondern auch die H-Atome in der Aminogruppe thermisch gelockert werden, spricht u.a. die experimentell gefundene Tatsache, dass der Zersetzungsdruck des Anilin- bzw. Toluidinchlorhydrats gerade beim Temperaturgebiet stark erhöht wird, wo die in Rede kommende Austauschreaktion merklich stattzufinden beginnt. Bei der Austauschreaktion im festen Zustand müssen wir weiter annehmen, dass die Anzahl und die Lage der sich an der Reaktion beteiligenden Kernwasserstoffatome hauptsächlich durch die geometrische Ordnung des Kristallgitters der betreffenden organischen Verbindungen bestimmt wird, weil sonst die beim vorliegenden Versuch festgestellte Tatsache kaum zu erklären ist, dass diese Anzahl des *p*-Toluidinchlorhydrats im

festen Zustand einen ganz anderen Wert besitzt als die Reaktion im geschmolzenen Zustand. Bei der Reaktion im geschmolzenen bzw. flüssigen Zustand, wo der Ordnungszustand des Kristallgitters ganz und gar verloren geht, wirkt für die Anzahl und die Lage der sich an der Reaktion beteiligenden Kernwasserstoffatome nur die Reaktionsfähigkeit der einzelnen H-Atome massgebend. So werden z.B. beim *p*-Toluidinchlorhydrat nicht nur die in *o*- und *o'*-Stellung befindlichen zwei H-Atome sondern auch die in *m*- und *m'*-Stellung befindlichen zwei H-Atome unter dem Einfluss der in *p*-Stellung befindlichen Methylgruppe in die Reaktion eingeführt. Dabei ist denkbar, dass die Reaktion oberhalb des Schmelzpunktes fast ausschliesslich intermolekular stattfindet, d.h. dass die Kernwasserstoffatome eines Moleküls gegen die H-Atome der Aminogruppe eines anderen Moleküls ausgetauscht werden, während bei der Reaktion, die unterhalb des Schmelzpunktes in der festen Phase stattfindet, ein Teil der Reaktion auch intramolekular stattfinden kann. So können z.B. das in *p*-Stellung befindliche Kernwasserstoffatome (des Anilinchlorhydrats) gegen das H-Atome der Aminogruppe des anderen benachbarten Moleküls, während die in *o*-Stellung befindlichen H-Atome gegen die H-Atome der Aminogruppe des eigenen Moleküls ausgetauscht werden.

Zum Schluss möchten wir Herrn Prof. T. Titani für seine freundlichen Ratschläge und seine Hilfe bei der vorliegenden Arbeit unseren herzlichsten Dank aussprechen. Der Nippon Gakujutsu-Shinkohkai (der Japanischen Gesellschaft für die Förderung der wissenschaftlichen Arbeit) sowie der Hattori Hohkohkai (der Hattori-Stiftung) für ihre finanzielle Unterstützung sind wir zu bestem Dank verpflichtet.

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Über die Reaktion von Grignardschen Reagenz auf α-Benzoyloxy-butyronitril.

Von Satoru KUWADA und Yosio SASAGAWA.

(Eingegangen am 8. September 1941.)

Im Anschluss an die Untersuchung über Stilben-Derivate haben wir[1] das Propioin durch Einwirkung von Überschuss Äthylmagnesiumbromid auf Propionaldehydcyanhydrin dargestellt. Es hat sich dabei gezeigt, dass die Ausbeute an Propioin durch den Reinheitsgrad des Cyanhydrins stark beeinflusst wird. Also haben wir als Ausgangsmaterial α-Benzoyloxy-butyronitril (I)[2] gewählt, welches sich in reinerem Zustand erhalten lässt.

Lässt man nun Äthylmagnesiumbromid auf α-Benzoyloxy-butyronitril (I) einwirken, so erhält man kein zu erwartenden Benzoyl-propioin bzw. dessen Ketiminsalz, sondern ein krystallinisches Produkt $C_{15}H_{23}O_2N$ (II) vom Schmp. 134.5°[3], welches offenbar durch Zusammentreten von zwei Molen Aethylmagnesiumbromid auf einem Mol α-Benzoyloxy-butyronitril zustande kam. Dieses Produkt ist in verd. Mineralsäuren unlöslich und nimmt beim Acylieren eine Acyl-Gruppe auf. Sowohl in konz. Salzsäure als auch in konz. Schwefelsäure löst es sich leicht auf, scheidet sich aber beim Verdünnen mit Wasser nichts aus.

Im gleichem Sinne liefert α-Benzoyloxy-butyronitril durch Einwirkung vom Phenylmagnesiumbromid ein Produkt $C_{23}H_{23}O_2N$ vom Schmp. 128° (III), welches sich gegen Reagentien genau so wie (II) verhält.

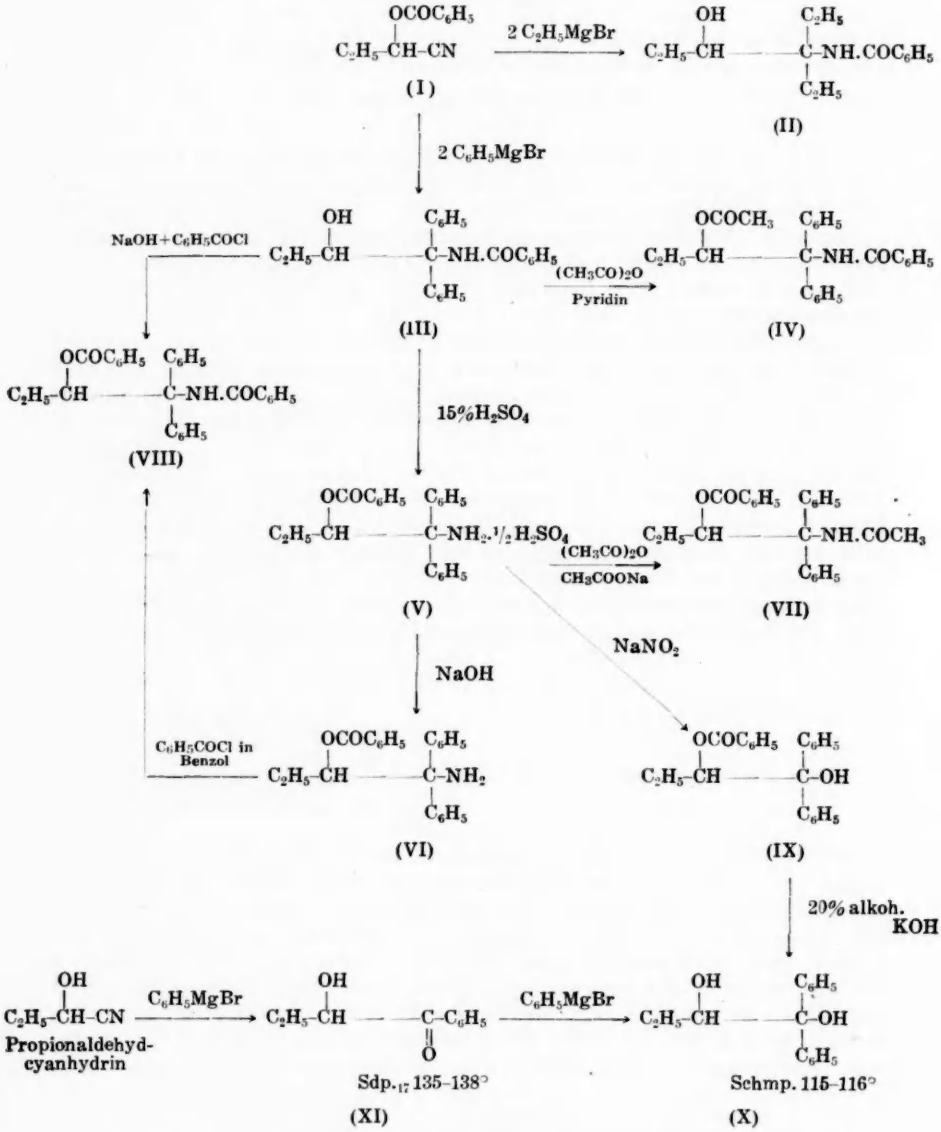
Vor kurzem haben Allen und Henze[4] berichtet, dass die Einwirkung von Allylmagnesiumbromid auf Äthoxy-acetonitril unter Bildung von einem Amin abnorm verläuft:

$$C_2H_5O-CH_2-CN + 2\,CH_2=CH-CH_2-MgBr \longrightarrow C_2H_5O-CH_2-\underset{\displaystyle CH_2-CH=CH_2}{\overset{\displaystyle NH_2}{\overset{|}{\underset{|}{C}}}}-CH_2-CH=CH_2$$

Zweifellos hat die Reaktion zwischen α-Benzoyloxy-butyronitril und Alkyl- bzw. Arylmagnesiumbromid in der ersten Phase, gleich wie die amerikanischen Forscher angaben, stattgefunden. Dass bei unserem Fall das Produkt keine basische Eigenschaft aufweist, ist darauf zurückzuführen, dass sich die Benzoyl-Gruppe am Hydroxyl zur benachbarten Amino-Gruppe umgelagert hat—eine schon häufig beobachtete Eigenschaft der Alkoholamine[5]. Erst durch Einwirkung von Säuren wird das neutrale N-Acylderivat unter Rückbildung von O-Acylderivat ins Aminsalz übergeführt. Also wollten wir die Einwirkung von Äthyl- bzw.

(1) *J. Pharm. Soc. Japan*, **60** (1940), 224.
(2) Francis und Davis, *J. Chem. Soc.*, **95** (1909), 1403.
(3) Alle Schmp. und Sdp. sind unkorrigiert.
(4) *J. Am. Chem. Soc.*, **61** (1939), 1790.
(5) Takeda, *J. Pharm. Soc. Japan*, **426** (1917), 1; Vinkler und Bruckner, *J. prakt. Chem.*, [2] **151** (1938), 17.

Phenylmagnesiumbromid auf α-Benzoyloxy-butyronitril und die Umwandlungen des Reaktionsproduktes (III) durch die folgenden Schemata ausdrücken:



Das aus (V) durch Diazotierung dargestellte Monobenzoat des Diphenyläthylglykols (IX) liefert beim alkalischen Verseifen das Glykol (X) vom Schmp. 115–116°, welches sich als identisch mit racem. 2-Aethyl-

2-oxy-l, 1-diphenyläthanol-1 von Roger[6] erwies. Derselbe Glykol (X) lässt sich auch aus Benzoyläthyl-carbinol (XI) vom Sdp.$_{17}$ 135–138° (aus Propionaldehydcyanhydrin und Phenylmagnesiumbromid[7]) und Phenylmagnesiumbromid darstellen. Da der Siedepunkt von (XI), im Gegensatz zum Benzoyläthylcarbinol (Sdp.$_9$ 143°) von Urion und Baum[8] erheblich niedriger und eher zu dem des Umlagerungsproduktes (Phenylpropionylcarbinols, Sdp.$_{11}$ 124–128° nach Urion und Baum) näher lag, so wäre es anzunehmen, dass unsere Verbindung (XI) schon eine Umlagerung in Phenylpropionylcarbinol erlitten hätte. Dass es aber nicht der Fall ist, ist daraus ersichtlich, da das Phenylpropionylcarbinol von Urion und Baum durch Einwirkung von Phenylmagnesiumbromid das bei 105–106° schmelzende α-2-Phenyl-1, 1-äthylphenyl-glykol[9] liefert. Auch haben wir durch Einwirkung des Äthylmagnesiumbromids auf Benzoin das β-2-Phenyl-1, 1-äthylphenyl-glykol[10] dargestellt, welches trotz des sehr naheliegenden Schmp. 116–117° in der Mischschmp.-Bestimmung mit unserem 2-Äthyl-1, 1-diphenyl-glykol (X) eine deutliche Depression zeigte. Also liegt daran kein Zweifel mehr, dass die Verbindung (XI) bei der Darstellung keine Umlagerung erlitten hat.

Hiermit wurde es gezeigt, dass Aldehydcyanhydrine auf Grignardschen Reagentien normaler Weise unter Bildung von Ketoalkoholen reagieren[7], während dessen O-Acyl-Verbindungen mit denselben Mitteln im Sinne der Allen-Henzeschen Reaktion N-Acyl-amine bilden.

Beschreibung der Versuche.

α-Benzoyloxy-butyronitril (I)[2]. 23.2 g. Propionaldehyd und 56 g. Benzoylchlorid wurden unter Umrührung in die eisgekühlten 250 c.c. Wasserlösung von 31.2 g. Cyankalium zugetropft und noch 4 Stdn. weiter umgerührt. Das Reaktionsprodukt wurde in Aether aufgenommen und der Aetherrückstand unter vermindertem Druck destilliert. Die Fraktion vom Sdp.$_{17}$ 157–158° beträgt 62.5 g. (82.7% d.Th.). Gefunden: C, 69.92; H, 5.72; N, 7.23. Berechnet für $C_{11}H_{11}O_2N$: C, 69.81; H, 5.86; N, 7.41%.

2-Äthyl-2-oxy-1,1-diäthyl-1-benzoylamino-äthan (II). In die Grignardschen Lösung, die aus 22 g. Äthylbromid, 5 g. Magnesiummetall und 150 c.c. abs. Aether dargestellt wurde, wurden 10 g. α-Benzoyloxybutyronitril zugetropft und 5 Stdn. auf dem Wasserbade umgerührt. Nach der Spaltung der Mg-Verbindung mit 20%iger Ammoniumchlorid wurde das Reaktionsprodukt mit Chloroform extrahiert. Durch Umlösen des Chloroformrückstands wurden farblose Nadeln vom Schmp. 133–134.5° erhalten. Ausbeute 3.7 g. Die Verbindung ist in Alkohol, Methanol, Aceton und Chloroform leicht löslich, in Aether und Benzol löslich, in Ligroin, Hexan und Petroläther schwer löslich, in kalter Salz-

(6) *Helv. chim. Acta*, **12** (1929), 1063.
(7) Asahina und Terasaka, *J. Pharm. Soc. Japan*, **494** (1923), 19; *Chem. Zentr.*, **1923** III, 434.
(8) *Chem. Zentr.*, **1939**, II, 3041.
(9) Tiffenau und Lévy, *Bull. soc. chim.*, **41** (1927), 1351.
(10) Tiffenau und Dorlencourt, *Compt. rend.*, **143** (1906), 127, 1243, *Ann. chim. phys.*, [8] **16** (1909), 237.

säure unlöslich. Erhitzt man sie mit 20%iger Schwefelsäure 40 Min., so löst sie in die Säure, aber beim Erkalten scheidet sich keine Substanz aus. Durch Verseifen mit 10%iger Kalilauge liefert sie Benzoesäure. Gefunden: C, 72.11; H, 9.09; N, 5.47. Berechnet für $C_{15}H_{23}O_2N$: C, 72.23; H, 9.30; N, 5.62%. Molekulargewichtsbestimmung nach Barger: 250±20. Ber. Mol.-Gew. 249.

Acetat: Dargestellt durch Behandlung mit Essigsäureanhydrid in Pyridin. Aus verd. Alkohol wurde es in Nadeln vom Schmp. 88–89° erhalten. Gefunden: C, 70.18; H, 8.42; N, 4.73. Berechnet für $C_{17}H_{25}O_3N$: C, 70.05; H, 8.65; N, 4.81%.

2-Äthyl-2-oxy-1,1-diphenyl-1-benzoylamino-äthan (III). In die Grignardschen Lösung, die aus 30 g. Brombenzol, 15 g. Magnesium und 50 c.c. abs. Aether dargestellt wurde, wurden 30 g. α-Benzoyloxybutyronitril eingetropft und gleich wie bei der Darstellung von (II) durchgeführt. Nach Umkrystallisieren aus Essigester-Petroläther des in Aether aufgenommenen Reaktionsprodukts erhielt man die farblose flache Nadeln vom Schmp. 127–128.5°. Ausbeute 48 g. (87.7% d.Th.). Die Verbindung ist in Aether, Methanol, Alkohol, Essigester, Aceton, Chloroform, Benzol und Dioxan leicht löslich, in Ligroin, Hexan und Petroläther schwer löslich. Gefunden: C, 79.76; H, 6.76; N, 4.19. Berechnet für $C_{23}H_{23}O_2N$: C, 79.96; H, 6.72; N, 4.06%.

Molekulargewichtsbestimmung nach Barger: 350±25. Ber. Mol.-Gew. 345.

Acetat (IV): Dargestellt durch Behandlung mit Essigsäureanhydrid in Pyridin. Farblose Tafeln vom Schmp. 149–152° (aus Methanol). Gefunden: C, 77.31; H, 6.66; N, 3.78. Berechnet für $C_{25}H_{25}O_3N$: C, 77.48; H, 6.51; N, 3.62%.

Benzoat (VIII): Die Verbindung (III) wurde in ca. 23%iger Kalilauge suspendiert und in der Kälte mit 2.5 g. Benzoylchlorid versetzt, dann noch 5 Stdn. umgerührt. Die mit Aether extrahierte ölige Substanz scheidet nach einem Monate Krystalle, die aus verd. Alkohol in farblose Nadeln vom Schmp. 146.5–148° bilden. Gefunden: C, 80.26; H, 5.88; N, 3.28. Berechnet für $C_{30}H_{27}O_3N$: C, 80.14; H, 6.06; N, 3.12%.

2-Äthyl-2-benzoyloxy-1,1-diphenyl-1-amino-äthan-schwefelsäuresalz (V). Die Verbindung (III) wurde mit 15%iger Schwefelsäure 2–3 Stdn. bis zur Auflösung erhitzt. Beim Stehenlassen scheiden sich daraus farblose Nadeln, die über 90° schmelzen, aber beim Waschen mit Wasser wird der Schmelzpunkt herabgedrückt.

2-Äthyl-2-benzoyloxy-1,1-diphenyl-1-acetylamino-äthan (VII). Das Schwefelsäuresalz (V) wurde mit Essigsäureanhydrid und Natriumacetat auf dem Wasserbad 3 Stdn. erwärmt. Das acetylierte Produkt wurde aus Ligroin umgelöst und die ausgeschiedene farblose feine Nadeln schmelzen bei 189–190°. Gefunden: C, 77.40; H, 6.81; N, 3.58. Berechnet für $C_{25}H_{25}O_3N$: C, 77.48; H, 6.51; N, 3.62%.

2-Äthyl-2-benzoyloxy-1,1-diphenyl-1-amino-äthan (VI). Das Schwefelsäuresalz (V) wurde mit 5%iger Natronlauge neutralisiert und die

ausgeschiedene krystallinische Substanz aus Alkohol umgelöst. Tafeln vom Schmp. 130–132°. Der Mischschmelzpunkt mit 2-Aethyl-2-oxy-1, 1-diphenyl-1-benzoylamino-äthan (III) (Schmp. 127–128.5°) liegt bei 109–117°. Gefunden: C, 79.82; H, 6.67; N, 4.47. Berechnet für $C_{23}H_{23}O_2N$: C, 79.96; H, 6.72; N, 4.06%.

Benzoat (VIII): 1 g. der Verbindung (VI) wurde mit 20 c.c. Benzol und 3 g. Benzoylchlorid 12 stündenlang auf dem Wasserbad erwämt. Das gebildete Benzoat wurde in Aether aufgenommen. Erst nach monatlangem Stehen scheiden sich aus dem Aetherrückstand Krystalle, die aus verd. Alkohol farblose Nadeln vom Schmp. 146.5–148° bilden. Eine Mischprobe mit dem Benzoat aus der Verbindung (III) zeigt keine Erniedrigung. Gefunden: C, 80.10; H, 5.88; N, 3.19. Berechnet für $C_{30}H_{27}O_3N$: C, 80.14; H, 6.06; N, 3.12%.

2-Äthyl-2-benzoyloxy-1,1-diphenyl-äthanol-1 (2-Äthyl-1,1-diphenyl-glykol-monobenzoat-2) (IX). 10 g. 2-Aethyl-2-benzoyloxy-1, 1-diphenyl-1-amino-äthan-schwefelsäuresalz (V) wurden im Gemisch von 30 c.c. Eisessig und 50 c.c. Wasser unter Eiskühlung mit dem Ueberschüss von kryst. Natriumnitrit versetzt, dann 2 Stdn. weiter umgerührt. Nach dem Behandlung der Reaktionslösung mit Harnstoff wurde die Aethanverbindung in Aether aufgenommen und aus Benzol umkrystallisiert. Seidenartige Nadeln vom Schmp. 149–152.5°. Ausbeute 5 g. Gefunden: C, 79.49; H, 6.39. Berechnet für $C_{23}H_{22}O_3$: C, 79.73; H, 6.41%

2-Äthyl-2-oxy-1,1-di henyl-äthanol-1 (2-Äthyl-1,1-diphenyl-glykol) (X). a) 1 g. der Verbindung (IX) wurde mit alkoholischer Kalilauge, die 2 g. Kaliumhydroxyd in 2 c.c. Wasser und 10 c.c. Alkohol enthält, 4 Stdn. auf dem Wasserbad erwärmt. Das mit Aether extrahierte Verseifungsprodukt krystallisiert aus Benzol-Petroläther in Rosetten der Nadeln vom Schmp. 115–116°. Gefunden: C, 79.32; H, 7.45. Berechnet für $C_{16}H_{18}O_2$: C, 79.29; H, 7.49%.

b) In die Grignardschen Lösung, die aus 31 g. Brombenzol, 5 g. Magnesium und 50 c.c. abs. Aether dargestellt wurde, wurden 5 g. Propionaldehydcyanhydrin zugetropft und unter Umrührung 5 Stdn. auf dem Wasserbad erwärmt. Nach dem Stehenlassen über Nacht wurde die Lösung mit 5% iger Schwefelsäure behandelt. Das mit Aether ausgezogene Substanz (XI) besitzt $Sdp._{17}$ 135–138°. Ausbeute 5.1 g. Dieses Oel wurde sofort mit Phenylmagnesiumbromid, das gleich wie oben dargestellt wurde, in Aether zur Grignardschen Reaktion gebracht, wodurch konnten wir farblose Nadeln vom Schmp. 115–116° aus Benzol-Petroläther, die mit obenerwähnten 2-Aethyl-2-oxy-1, 1-diphenyl-äthanol-1, d.h. racem. 2-Äthyl-2-oxy-1, 1-diphenyl-äthanol-1 von Roger[9] identisch ist. Gefunden: C, 79.11; H, 7.66. Berechnet für $C_{16}H_{18}O_2$: C, 79.29; H, 7.49%.

β-Äthyl-hydrobenzoin (β-2-Phenyl-1,1-äthylphenyl-glykol). 10 g. Benzoin wurden portionsweise in die Grignardschen Lösung, die aus 22 g. Aethylbromid, 5 g. Magnesium und 200 c.c. abs. Aether dargestellt wurde, zugetropft und 4 Stdn. auf dem Wasserbad umgerührt. Nach dem

Spalten der Magnesiumverbindung mit 20%igem Ammoniumchlorid wurde das Reaktionsprodukt mit Aether extrahiert und aus Alkohol umgelöst. Seidenartige Nadeln vom Schmp. 116–117°. Ausbeute 10.3 g.

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Studies on the Reactions between Oxides in Solid State at Higher Temperatures. I. The Reaction between Magnesium Oxide and Titanium Oxide.*

By **Yasuo TANAKA.**

(Received September 16, 1941.)

Introduction. From an early date, reactions in solid state, especially those between certain oxides at relatively high temperatures, have widely been used practically in the ceramic or the silicate industry, in the production of catalysts and pigments as well as in the various branches of chemical industry. Nevertheless, there have been a rather few scientific researches in this branch of chemistry. Although these reactions have recently become the object of a number of investigators, it is still desirable that more experimental results will be accumulated. The author has been studying for several years the addition reactions with the powder mixtures between a group of basic and of acidic oxides in the solid state, and the results will be published in a series of forthcoming papers.

By the reaction in solid state, the product is at first in an amorphous state, from which the new compound crystallizes out easily, when the reaction temperature is sufficiently high. At the lower temperature, the crystal growth is difficult, and this amorphous state is particularly active as a solid catalyst.(1) But the main object of the present series of investigation is not to discuss about this amorphous state. The experiments have been carried on in the temperature range so high that the reaction products may be considered to crystallize out comparatively easily. The present paper deals with the reaction between magnesium oxide and titanium oxide.

The reaction between magnesium oxide and titanium oxide was first studied by Hautefeuille.(2) He obtained magnesium ortho- and metatitanate ($2MgO{\cdot}TiO_2$ and $MgO{\cdot}TiO_2$) by fusing titanium oxide to-

* A summarized translation of the papers published in Japanese in *J. Chem. Soc. Japan*, **59** (1938), 1412 (preliminary report); **60** (1939), 212, 314, 949.

(1) *Cf.*, for instance, J. A. Hedvall, "Reaktionsfähigkeit fester Stoffe," 146, Leipzig (1938); G. F. Hüttig, *Z. angew. Chem.* **49** (1936), 882.

(2) P. Hautefeuille, *Ann. chim. phys.*, [4], **4** (1865), 169.

gether with magnesium chloride, and their densities were mentioned as 3.52 and 3.91, respectively. Wartenberg and Prophet[3] studied the fusion curve of the system magnesium oxide and titanium oxide and obtained two maxima, corresponding to the melting points of $2MgO{\cdot}TiO_2$ and $MgO{\cdot}2TiO_2$ (dititanate). Büssem, Schusterius and Ungewiss[4] studied röntgenographically the reaction products between magnesium oxide and titanium oxide at 1460° and confirmed the existence of the three titanates, $2MgO{\cdot}TiO_2$, $MgO{\cdot}TiO_2$ and $MgO{\cdot}2TiO_2$. Tammann[5] reported that the "reaction temperature" between magnesium oxide and titanium oxide in solid state was 725°. Jander[6] suggested that, in the solid reaction, $2MgO{\cdot}TiO_2$ was formed most easily among the three titanates. However, in studying the effect of titanium oxide on the sintering of magnesite, the present author[7] found that $MgO{\cdot}TiO_2$ was formed more readily than $2MgO{\cdot}TiO_2$ even in a mixture of $MgO:TiO_2=2:1$.

As it is a very interesting problem, which of the compounds is formed at first by a reaction between solid substances where two or more addition compounds can be present,[6][8] the present experiment has been commenced mainly to make clear the order of formation of the three titanates in this reaction. In the meanwhile, Jander and Bunde[9] have studied the solid reaction of this system by the X-ray method and reported that $MgO{\cdot}TiO_2$ was formed at first, whatever the mixing ratio of the two components might be, and that, while $MgO{\cdot}2TiO_2$ was formed comparatively easily, the formation of $2MgO{\cdot}TiO_2$ was very difficult. As for the fact that $2MgO{\cdot}TiO_2$ is difficult to be formed, the result of the following experiment agrees with that of Jander and Bunde, but as for the order of formation of $MgO{\cdot}TiO_2$ and $MgO{\cdot}2TiO_2$, the conclusion of the two experiments are different.

Besides, it has been known that many solid reactions can be influenced by water vapour and other gases.[10] Especially, as studied throughly by Tamaru and Andô,[11] the reaction between calcium oxide and stannic oxide is accelerated remarkably by the traces of reducing gases due to the reduction of stannic oxide. As titanium oxide is comparatively easily reduced into lower oxides,[12] it is expected that a reducing atmosphere may also have an accelerating effect upon the present reaction, and the author has actually found this effect, qualitatively. However, this problem was not treated in the present research. The experiments were carried out in a current of dry air.

I. Reaction products at 1400°. In order to confirm the kinds of the addition compounds formed by the solid reaction between MgO and

(3) H. v. Wartenberg and E. Prophet, *Z. anorg. allgem. Chem.*, **208** (1932), 369.
(4) W. Büssem, C. Schusterius and A. Ungewiss, *Ber. deut. keram. Ges.*, **18** (1937), 433.
(5) G. Tammann, *Z. anorg. allgem. Chem.*, **149** (1925), 68.
(6) W. Jander, *Z. Angew. Chem.*, **49** (1936), 879.
(7) *J. Soc. Chem. Ind., Japan*, **42** (1939), 387, 202B.
(8) W. Jander, *Z. Angew. Chem.*, **47** (1934), 235.
(9) W. Jander and K. Bunde, *Z. anorg. allgem. Chem.*, **239** (1938), 418.
(10) *Cf.* J. A. Hedvall, *loc. cit.*, 157, 204, 211 etc.
(11) S. Tamaru and N. Ando, *Z. anorg. allgem. Chem.*, **184** (1929), 385; **195** (1931), 309; *J. Chem. Soc. Japan*, **52** (1931), 36, 107.
(12) N. Nasu, *Science Repts. Tohoku Imp. Univ.* Ser. I, **25** (1936), 510; *J. Chem. Soc. Japan*, **56** (1935), 542, 659.

TiO_2 and to know their properties, uniform mixtures of various proportions of MgO and TiO_2 were pressed into small cylindrical bodies and heated at 1400° for 10 hours in a platinum boat; the densities of the reaction products were measured, they were studied by the X-ray method, and the compositions of them were determined analytically. As the lowest eutectic point of this system has been reported as 1625°[3], it might be sure that at 1400° the reaction proceeded in solid state without any formation of a liquid phase.

MgO used was the "Shika, extra pure", and TiO_2 was a "Kahlbaum" preparation; both of them were very fine powders. TiO_2 has three modifications, and it has been known that the preparation obtained from a solution is in anatase modification, and on heating, it changes irreversibly to rutile.[13] Their densities are 3.840 and 4.239, resepectively. The density of TiO_2 used here was 3.839, and it changed to 4.163 when heated at 1200° for 5 hours.

As shown in Table 1, the densities of the reaction products are always smaller than those of the mechanical mixtures of the corresponding composition, and as three singular points are found at $MgO:TiO_2=2:1$, 1:1 and 1:2, it is readily supposed that the three titanates corresponding to the above compositions are formed.

Table 1. Densities and compositions of the reaction products at 1400°. §

No. of sample	Mixing ratio $MgO:TiO_2$	Density	Composition (%)				
			MgO	$2MgO\cdot TiO_2$	$MgO\cdot TiO_2$	$MgO\cdot 2TiO_2$	TiO_2
1	—	3.493	100.0				
2	20 : 1	3.494	82.5	16.1	0.9	0.5	0.0
3	6 : 1	3.511	50.9	47.2	1.1	0.9	0.0
4	3 : 1	3.532	21.7	76.5	0.9	1.5	0.0
5	2 : 1	3.541	3.0	89.0	6.5	1.4	0.0
6	3 : 2	3.656	2.4	54.3	35.2	8.1	0.0
7	1 : 1	3.856	1.9	2.0	84.7	11.3	0.0
8	2 : 3	3.682	1.9	1.6	21.2	77.3	0.0
9	1 : 2	3.610	2.0	0.2	2.4	85.3	10.1
10	1 : 5	3.915	1.9	0.4	0.3	34.7	62.7
11	—	4.225					100.0

§ Mixing of the components and calculation of the compositions were carried out under the assumption that the two preparations were completely pure (ignition losses being considered).

This was confirmed by the X-ray method. At the same time, it was proved that in the reaction products TiO_2 was in the rutile modification. It seemed that there existed no appreciable amount of solid solutions between these compounds. The lattice constants of $2MgO\cdot TiO_2$, $MgO\cdot TiO_2$

(13) *Cf.* J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VII, 37, London (1927).

and TiO_2 are shown in Table 2, which are all in good agreement with the data hitherto given. The interference lines of $MgO{\cdot}2TiO_2$ are given in Table 3; the crystal structure of which is not certain.

Table 2. Lattice constants.

Crystal	Crystal form	Lattice constant	
		observed here	hitherto given
$2MgO{\cdot}TiO_2$	Cubic (Spinel str.)	$a = 8.42$Å	a=8.41Å ;[14] 8.413Å[4]
$MgO{\cdot}TiO_2$	Hexagonal (Rhombohedral)	$a = 5.46$Å, $\alpha = 55.0°$	a=5.40Å, α=55°1′[15] ; a=5.54Å, α=54°39′[16]
TiO_2 (Rutile)	Tetragonal	$a = 4.58$Å, $c = 2.95$Å	a=4.58Å, c/a=0.66₄[17]

Table 3. Interference lines of $MgO{\cdot}2TiO_2$

Intensity §	sin θ §§	Intensity §	sin θ §§
w	0.195	vw	0.570
vw	0.248	w	0.582₅
st	0.276₅	m	0.628
vw	0.339	w	0.682
st	0.354	vw	0.737
w	0.401	w	0.771₅
w	0.437	w	0.781
m	0.495	vw	0.876
m	0.519₅		
w	0.556		

§ Roughly estimated as very strong, strong, medium, weak and very weak.

§§ For K_α and K_β lines of iron.

The determination of the compositions of the reaction products were carried out as follows:—To the finely pulverized sample was added 10 parts of a 20% ammonium chloride solution, and it was warmed on a water-bath for 40 minutes, while stirred constantly. The amount of MgO dissolved was regarded as free magnesium oxide. A 10% ammonium

(14) Tom. F. W. Barth and E. Posnjak, *Z. Krist.*, **82** (1932), 325.

(15) Wm. H. Zachariasen, *Skrifter Norske Videnskaps-Akad. i Oslo*, **1**, (1928), 7; *Chem. Abstracts*, **23** (1929), 1790.

(16) T. Barth and E. Posnjak, *Z. Krist.*, **88** (1934), 265, 271.

(17) *Cf.* R. Glocker, "Materialprüfung mit Röntgenstrahlen," 2. Aufl., 240, Berlin (1936).

chloride solution, used by Büssem and coworkers,[4] was proved too dilute. By a similar treatment, it was proved that, $2MgO \cdot TiO_2$ was completely soluble in 4 N hydrochloric acid with a trace of $MgO \cdot TiO_2$, and that all the $MgO \cdot TiO_2$ with a small part of $MgO \cdot 2TiO_2$ was dissolved in 12 N hydrochloric acid, while the major part of $MgO \cdot 2TiO_2$ and free TiO_2 were insoluble even in concentrated hydrochloric acid. Therefore, by determining the solubility of each sample in these three reagents, it is possible to calculate the amounts of the three titanates formed and of free MgO and TiO_2. The results are also given in Table 1.

From these experiments it is obvious that three titanates,

Magnesium orthotitanate	$2MgO \cdot TiO_2$
Magnesium metatitanate	$MgO \cdot TiO_2$,
Magnesium dititanate	$MgO \cdot 2TiO_2$,

are formed by the solid reaction between MgO and TiO_2 at 1400°; the purity of each of the three titanates obtained from the equivalent mixtures is 85–90%.

II. Course of the reaction between 780° and 1200°. The pressed cylinders of the mixtures corresponding to the three titanates, i.e., MgO: TiO_2=1:2, 1:1 and 2:1, and, as a case of excess MgO, a mixture of MgO: TiO_2=6:1 were heated at 1000° and 1200°, and in some instances at 780° and 900° also, for various durations of time; the course of reaction was followed by determining the compositions of the products analytically,* and the results were checked by the X-ray method.

The mixtures used for the reactions at 1000° and 1200° were heated previously to 600° to remove possible traces of hydroxide and carbonate of magnesium and kept in a desiccator; those used at 780° and 900° were treated at 400°, (because it was proved that at 600° the reaction might somewhat take place). The experiments were carried out in a platinum furnace fitted with a potentiometric temperature regulator. As already mentioned, a constant current of air, carefully dried with phosphorus pentoxide, was passed through the reaction tube during the experiments.

The compositions of the reaction products are given in Tables 4–7, and in some instances, they are graphically plotted in Figures 1–3. (In acid treatment, the solubilities of $MgO \cdot TiO_2$ and $MgO \cdot 2TiO_2$ in 4 N and

Table 4. Course of the reaction, $MgO : TiO_2 = 1 : 2$.

Reaction temperature	Time (hrs.)	Composition of the products (%)			
		MgO	$MgO \cdot TiO_2$	$MgO \cdot 2TiO_2$	TiO_2
780°	0.5	15.1	4.8	16.8	63.2
	1	14.0	6.9	18.8	60.2
	3	12.0	11.6	20.8	55.6
	6	10.9	11.6	26.3	51.2
900°	0.5	7.8	13.7	38.2	40.3
	1	6.8	14.6	41.7	36.9
	3	4.7	15.8	50.6	29.0
	6	4.0	11.9	60.0	24.0

* There are only two or three instances of solid reaction whose courses have been studied analytically.

Table 4.—(*Concluded*)

Reaction temperature	Time (hrs.)	Composition of the products (%)			
		MgO	$MgO \cdot TiO_2$	$MgO \cdot 2TiO_2$	TiO_2
1000°	0.5	5.4	4.8	65.5	24.3
	1	4.3	5.3	69.9	20.6
	3	3.3	9.2	68.0	19.4
	6	3.3	7.8	70.4	18.5
1200°	0.5	3.7	0.3	80.9	15.1
	1	3.4	0.6	82.3	13.7
	3	3.1	0.6	83.5	12.8
	6	2.9	0.5	84.9	11.7
	12	2.4	0.6	87.1	10.0

Table 5. Course of the reaction, $MgO : TiO_2 = 1 : 1$.

Reaction temperature	Time (hrs.)	Composition of the products (%)			
		MgO	$MgO \cdot TiO_2$	$MgO \cdot 2TiO_2$	TiO_2
780°	0.5	26.3	11.6	16.4	45.6
	1	25.3	13.7	18.4	42.6
	3	21.8	25.0	16.4	36.8
	6	19.3	33.1	15.4	32.2
900°	0.5	16.7	28.3	36.2	18.8
	1	12.2	43.5	33.3	11.0
	3	8.3	62.6	20.8	8.3
	6	7.4	65.8	20.3	6.6
1000°	0.5	10.4	36.5	53.2	0.0
	1	8.3	49.8	41.9	0.0
	3	4.8	71.1	24.1	0.0
	6	3.7	78.1	18.3	0.0
1200°	0.5	3.6	78.7	17.2	0.5
	1	3.7	80.2	14.3	1.8
	3	3.1	81.4	15.2	0.3
	6	2.8	83.5	13.8	0.0
	12	2.6	84.1	13.1	0.0

Table 6. Course of the reaction, $MgO : TiO_2 = 2 : 1$.

Reaction temperature	Time (hrs).	Composition of the products (%)				
		MgO	$2MgO \cdot TiO_2$	$MgO \cdot TiO_2$	$MgO \cdot 2TiO_2$	TiO_2
1000°	0.5	28.5	0.0	54.3	17.5	0.0
	1	27.5	0.0	61.1	11.4	0.0
	3	27.1	0.0	62.7	10.2	0.0
	6	26.0	4.0	60.5	9.5	0.0
1200°	0.5	22.1	15.9	57.2	4.4	0.4
	1	21.3	18.2	57.3	3.0	0.2
	3	15.7	39.4	42.3	2.6	0.0
	6	12.8	49.7	36.1	1.4	0.0
	12	11.6	54.7	32.2	1.5	0.0

Table 7. Course of the reaction, $MgO : TiO_2 = 6 : 1$.

Reaction temperature	Time (hrs.)	Composition of the products (%)				
		MgO	$2MgO \cdot TiO_2$	$MgO \cdot TiO_2$	$MgO \cdot 2TiO_2$	TiO_2
1000°	0.5	63.8	0.0	30.4	5.8	0.0
	1	63.1	0.0	35.0	2.0	0.0
	3	63.1	0.0	34.9	2.0	0.0
	6	62.4	2.0	34.6	1.0	0.0
1200°	0.5	51.4	45.8	1.8	1.0	0.0
	1	50.9	46.7	2.4	0.0	0.0
	3	51.1	46.1	2.4	0.4	0.0
	6	50.6	47.9	1.5	0.0	0.0
	12	50.4	48.7	0.9	0.0	0.0

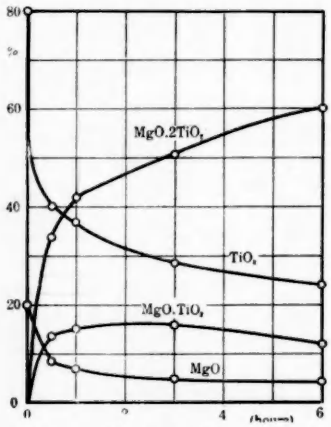

Fig. 1. Course of the reaction, $MgO : TiO_2 = 1 : 2$ at 900°.

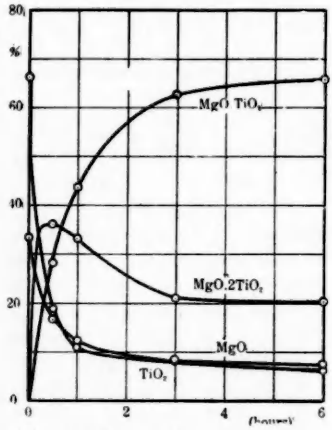

Fig. 2. Course of the reaction, $MgO : TiO_2 = 1 : 1$ at 900°.

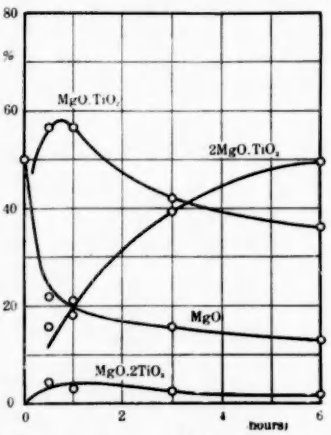

Fig. 3. Course of the reaction, $MgO : TiO_2 = 2 : 1$ at 1200°.

12 N HCl, respectively, were proved to increase with the decreasing reaction temperature. This might be attributed to the incompleteness of the crystal growth of the two titanates, i.e., to the existence of the amorphous reaction product, but the existence of the solid solutions might also be suspected.) With a mixture, $MgO : TiO_2 = 1 : 2$, it is obvious that the main reaction product is always $MgO \cdot 2TiO_2$; and it can be interpreted that some $MgO \cdot 2TiO_2$ accompanied is formed locally where MgO exists in excess, because the mixing of the components could never be completely homogeneous. In the case of $MgO : TiO_2 = 1 : 1$, while at the early stage

of the reaction there exists more $MgO{\cdot}2TiO_2$ than $MgO{\cdot}TiO_2$, the ratio of the two titanates is reversed as the reaction proceeds, and finally $MgO{\cdot}TiO_2$ becomes the main reaction product. So it may easily be recognized that the initial reaction product in this case is also $MgO{\cdot}2TiO_2$, and $MgO{\cdot}TiO_2$ is formed by the further reaction between $MgO{\cdot}2TiO_2$ thus obtained and the excess MgO. $2MgO{\cdot}TiO_2$ is never found in this mixture. This compound is very difficult to be formed, and in a stoichiometric mixture it is formed at 1200° at length, but the reaction is hardly completed at this temperature. With the mixtures of a large excess of MgO, e.g., $MgO:TiO_2=6:1$, the formation is easily completed at 1200°. The results of the röntgenographic studies agree with these results.

From these results it could be concluded that, by the reaction between MgO and TiO_2 in solid state, the first reaction product is $MgO{\cdot}2TiO_2$, whatever the mixing ratio of the two components might be; when an excess of MgO is present, $MgO{\cdot}TiO_2$ is formed gradually; and while $2MgO{\cdot}TiO_2$ is formed similarly, the velocity of its formation is very slow in the temperature range observed here. The reaction consists of the following three consecutive reactions:

$$MgO + 2TiO_2 \rightarrow MgO{\cdot}2TiO_2,$$
$$MgO{\cdot}2TiO_2 + MgO \rightarrow MgO{\cdot}TiO_2$$
$$MgO{\cdot}TiO_2 + MgO \rightarrow 2MgO{\cdot}TiO_2.$$

III. Influence of the experimental conditions on the course of reaction. The conclusion about the order of the formations of $MgO{\cdot}TiO_2$ and $MgO{\cdot}2TiO_2$ differs, as previously stated, in the above experiment and in the experiment of Jander and Bunde.[9] As this may be due to the difference in some of the experimental conditions, the experiments were repeated under various conditions.

(1) *The reaction in loose powder form with TiO_2 in rutile modification*:— In the experiment of Jander Bunde, TiO_2 was heated to 800° before use, and they stated that the preparation thus obtained was in rutile modification*, and the reaction was carried out with powder mix-

Table 8. Reaction in powder form with rutile.

Mixture	Reaction temperature	Time (hrs.)	Composition of the products (%)			
			MgO	$MgO{\cdot}TiO_2$	$MgO{\cdot}2TiO_2$	TiO_2
$MgO:TiO_2=1:2$	1000°	0.5	15.7	0.0	21.8	62.5
		3	12.0	1.5	37.7	48.8
	1200°	1	5.1	0.0	74.4	20.4
$MgO:TiO_2=1:1$	1000°	0.5	30.2	0.0	16.4	53.4
		3	28.5	0.9	23.3	47.2
	1200°	1	15.8	10.4	70.6	3.1

* Although 915°, given by A. Schröder [*Z. Krist.*, **66** (1928), 493], may be regarded as the most probable transition temperature of anatase into rutile, under certain conditions rutile seems to be obtained already at as low as 800°.

tures in loose form. To compare with their experiment, the reaction experiment in loose powder form was made at 1000° and 1200° by using the TiO_2 preparation previously heated to 1200°, i.e., rutile. MgO, too, was used after the same heat treatment. The results are given in Table 8, which lead to a conclusion, more distinctly than the results in the last paragraph; that $MgO{\cdot}2TiO_2$ is the first reaction product. It goes without saying that the whole reaction proceeds slowly.

(2) *The reaction in loose powder form with anatase*:— The experiment in loose powder form with TiO_2 preparation used in the last paragraph, i.e., anatase, was also made. As shown in Table 9, although the reaction proceeds slowly, the course of the reaction is quite identical as before.

Table 9. Reaction in powder form with anatase, 1000°.

Mixture	Reaction time (hrs.)	Composition of the products (%)			
		MgO	$MgO{\cdot}TiO_2$	$MgO{\cdot}2TiO_2$	TiO_2
$MgO : TiO_2 = 1 : 2$	0.5	7.2	11.9	44.6	36.4
	3	4.4	8.6	63.9	23.2
$MgO : TiO_2 = 1 : 1$	0.5	13.5	19.4	67.1	0.0
	3	8.3	50.7	41.0	0.0

(3) *Influence of water vapour*:— It has been already cited that, in some instances, the influence of water vapour on the solid reaction is remarkable.[10] Although in the present experiment, this influence is always excluded carefully, Jander and Bunde touched nothing on this problem. Therefore, by way of precaution, an experiment to confirm this influence was carried out. A constant current of air was passed through a water reservoir at 98° and then into the reaction vessel; other experimental conditions were the same as in paragraph II. The results

Table 10. Influence of water vapour, 1000°.

Mixture	Reaction time (hrs.)	Composition of the products (%)			
		MgO	$MgO{\cdot}TiO_2$	$MgO{\cdot}2TiO_2$	TiO_2
$MgO : TiO_2 = 1 : 2$	0.5	5.6	6.4	61.5	26.5
	3	3.0	8.7	70.4	17.9
$MgO : TiO_2 = 1 : 1$	0.5	8.2	50.7	41.1	0.0
	3	4.7	71.1	24.2	0.0

are given in Table 10; and it shows that, although the reaction seems to be slightly accelerated by the presence of water vapour, the course of the reaction in this case is also unchanged.

As seen from these experiments, the reaction proceeds, under various experimental conditions, in the same manner, and $MgO{\cdot}TiO_2$ could never

be regarded as the first reaction product. Therefore, it can be concluded that, in general cases or—if it is permitted to use the word "normal experimental condition" as Jander[18] has previously used—under normal conditions, the course of the solid reaction between MgO and TiO_2 is as above mentioned, and even if $MgO{\cdot}TiO_2$ happens to be formed at first, it must be under special conditions.

IV. The reaction $MgO{\cdot}TiO_2+TiO_2$ and $MgO{\cdot}2TiO_2+MgO$. The reactions between $MgO{\cdot}TiO_2$ and TiO_2, and $MgO{\cdot}2TiO_2$ and MgO at 900° were studied further. The results of the experiments together with the purities of the two titanates used are shown in Tables 11 and 12.

Table 11. The reaction $MgO{\cdot}TiO_2+TiO_2$ at 900°.

Reaction time (hrs.)	Composition (%)			
	MgO	$MgO{\cdot}TiO_2$	$MgO{\cdot}2TiO_2$	TiO_2
(sample)	2.9	81.8	15.3	0.0
0	1.7	48.9	9.1	40.3
1	1.8	28.6	43.1	26.5
3	1.6	14.7	67.4	16.4
6	1.7	13.7	68·9	15.8

Table 12. The reaction $MgO{\cdot}2TiO_2+MgO$ at 900°.

Reaction time (hrs.)	Composition (%)			
	MgO	$MgO{\cdot}TiO_2$	$MgO{\cdot}2TiO_2$	TiO_2
(sample)	2.1	0.3	88.8	8.8
0	18.5	0.2	74.0	7.3
1	14.7	17.0	64.9	3.4
3	12.4	27.1	59.5	1.0
6	12.2	28.3	58.5	1.0

The reaction between $MgO{\cdot}TiO_2$ and TiO_2 to form $MgO{\cdot}2TiO_2$ proceeds more easily than the formation of $MgO{\cdot}TiO_2$ from $MgO{\cdot}2TiO_2$ and MgO. From these facts, too, it is readily anticipated that $MgO{\cdot}2TiO_2$ is the first reaction product by the solid reaction between MgO and TiO_2.

V. Mechanism of the reaction. In order that a reaction takes place actually between solid substances, it is necessary first of all that a part of the atoms (or atom groups) of the components is in a deviated position from the normal crystal lattice, i.e., in a state of disorder.[19]

(18) W. Jander and E. Hoffmann, *Z. anorg. allgem. Chem.*, **218** (1934), 211.

(19) *Cf.* W. Jost, "Diffusion und chemische Reaktion in festen Stoffen," 39, Dresden and Leipzig (1937).

Then, at the contact surface of the two components, these atoms may exchange with each other, forming an amorphous layer of the mixture of them, and from which a new reaction product crystallizes out easily so long as the reaction temperature is high enough.[1][6]

When a crystalline film of the reaction product is formed, further reaction is only possible by the diffusion of the two components through this film. Which of the components diffuses chiefly, depends on the nature of the reaction. By the reaction of silicate formation, it is believed that the basic oxide, e.g. MgO, diffuses[6][18]; by the spinel formation, Hild[20] has regarded that the basic oxide diffuses, while others[21] have considered *vice versa*. Wagner[22] has suggested that in ion crystals the smaller cation diffuses generally, and this supposition was proved for the reaction: $2AgI + HgI = Ag_2HgI_4$[23], where equivalent quantities of Ag^+ and Hg^{++} ions are exchanged in Ag_2HgI_4 phase, and Ag_2HgI_4 is formed newly at the two boundaries, AgI/Ag_2HgI_4 and Ag_2HgI_4/HgI_2. He has presented analogous interpretation for the formation of spinels and silicates.[22]

From these points of view, it may be admitted for the mechanism of the present reaction that, at the contact surface of magnesium oxide and titanium oxide, an amorphous layer of these mixtures is formed at first, the amount of which is not so much, within the temperature range observed here, from which the stable reaction product (in this case $MgO{\cdot}2TiO_2$) crystallizes out easily; and further reaction proceeds by the diffusion of the two components—probably in the form of Mg^{++} and Ti^{++++} ions—through this phase. Further discussions about the amorphous layer at the early stage of the reaction and the diffusion component are abridged here.*

As repeatedly stated, the first reaction product in this reaction is always $MgO{\cdot}2TiO_2$. About the problem which compound is formed at first by a reaction between solid substances in which many addition compounds can be formed, the relation is very complicated. For the formation of silicates, Jander[6][18] has considered that the relative difficulty of the formation depends chiefly on the crystal structure of the addition compounds, namely, as the crystal structure of orthosilicates with tetrahedral SiO_4-group may be regarded as simple compared with the structure of metasilicates with long fibrous structure as -Si-O-Si-, the former crystallizes more readily from the amorphous layer and is formed at first. Contrary to Jander, Wagner[22] has considered that, as the diffusion in orthosilicates is easier than in metasilicates, even if both silicates are formed equally at the beginning of the reaction, metasilicate layer does not build up, and only the amount of orthosilicates increases; the relation is just as in the oxidation of metals where many oxide layers can be formed. At any rate, as it may be understood, the relative difficulty of

(20) K. Hild, *Z. physik. Chem.*, A, **161** (1936), 317.

(21) W. Jander and W. Stamm, *Z. anorg. allgem. Chem.*, **199** (1931), 165; G. Hüttig and E. Zeidler, *Kolloid-Z.*, **75** (1936), 170.

(22) C. Wagner, *Z. physik. Chem.*, B, **34** (1936), 309.

(23) E. Koch and C. Wagner, *ibid.*, **34** (1936), 317.

* Recently, W. Jander and G. Leuthner have studied about the amorphous reaction product between MgO and TiO_2. [*Z. anorg. allgem. Chem.*, **241** (1939), 57.]

diffusion in crystals also depends upon their crystal structures—for instance, the diffusion in orthosilicates with simple constitution is easier than in metasilicates with complicated fibrous structure—, crystals of simple structure can be found from either argument at the early stage of the reaction.

In the present case, although the crystal structure of $MgO{\cdot}2TiO_2$ is not certain, when it is permitted to assume that the crystal structure of $MgO{\cdot}2TiO_2$ is more simple than that of $MgO{\cdot}TiO_2$ and of $2MgO{\cdot}TiO_2$, it may be considered that $MgO{\cdot}2TiO_2$ crystallizes out most easily from the amorphous layer, and, even if other compounds are formed at the same time, they do not build up. Thus it is well interpreted that $MgO{\cdot}2TiO_2$ is the first reaction product. As the reaction proceeds and the thickness of $MgO{\cdot}2TiO_2$ layer increases, the diffusion in this layer becomes gradually difficult, and $MgO{\cdot}TiO_2$ begins to be formed at the contact surface of $MgO{\cdot}2TiO_2$ and MgO. $2MgO{\cdot}TiO_2$ is formed also in the same way, but with great difficulty.

By the solid reaction, if the diffusion process takes place slowly enough compared with the surface reaction, which is just so in most cases, the rate of the whole reaction is controlled only by the diffusion,[24] and there exists an approximate relation between the thickness of the reaction product (ξ) and the reaction time (t):[25]

$$d\xi/dt = k'/\xi \qquad \text{or} \qquad \xi^2 = 2k't + C'.$$

By the reaction with powder mixtures, it is impossible to determine directly the thickness of the layer of the product, and it is the amount of the product formed, or of the components reacted (x) which can be measured; therefore, in order to apply the above relation to this case, the relation between them should be known. Jander[26] has derived the following relation, by assuming that the reaction proceeds uniformly on a spherical substance with a radius of r:

$$1-\sqrt[3]{1-x} = \xi/r,^*$$

and so

$$\{1-\sqrt[3]{1-x}\}^2 = 2kt + C.$$

Although this relation holds strictly for a substance in a small amount, through which another substance in large excess diffuses, it can also be applied approximately, at least in the early stage of the reaction, to a mixture of any mixing ratio, and it has been proved for the reactions between barium carbonate and silica, etc.[26][6]

It was tried to apply the relation to the result of the present experiment, and the relation between $\{1-\sqrt[3]{1-x}\}^2$ and the reaction time was plotted for the mixture corresponding to the first reaction product,

(24) *Cf.* W. Jost, *loc. cit.*, 180.
(25) H. Braune, *Z. physik. Chem.*, **110** (1924), 147.
(26) W. Jander, *Z. anorg. allgem. Chem.*, **163** (1927), 1.
* x is expressed as the fraction of the original amount of the component.

i.e., $MgO:TiO_2=1:2$, in paragraph II. As the measured points fall on a straight line so long as the reaction temperature is not so high and the reaction proceeds not so far, it is recognized that the main part of the reaction is controlled by diffusion, but the line does not fall on the origin, showing that there exists a notable rapid initial reaction. It is natural that the above relation does not hold when the reaction proceeds too far.

For the rapid initial reaction, the following considerations may be given at present: as the reaction is exothermic,** at the beginning of the reaction, the true reaction temperature becomes inevitably higher than the furnace temperature, and, as the experiment has been carried out with pressed bodies of the mixtures of very fine powders, the surface reaction proceeds to a considerable amount. A similar initial reaction has been reported by Ward and Struthers[27] in the reaction between barium carbonate and ferric oxide.

The values of k for the diffusion process of $MgO{\cdot}2TiO_2$ formation can be roughly represented in terms of

$$k = A\ e^{-Q/RT},$$

or

$$k = 3.9\times10^4\ e^{-36{,}000/RT},$$

where Q may be regarded as the energy of activation in calories per mole of the diffusion.

As shown in Table 13, the value of Q is the same order as those which have been known in other solid reactions, and is also similar to those of the comparatively well studied diffusion processes between metals.[31]

Table 13. Energies of activation of the solid reactions.

Reaction	Mixing ratio	Product	Q (Kcal./mole)
$BaCO_3 + SiO_2$	1 : 10	Ba_2SiO_4 ?	50.2[26], 40.7[28]
,,	1 : 1	,,	42.6[29]
$CaO + SiO_2$	1 : 1	Ca_2SiO_4	32.2[29]
$BaCO_3 + Fe_2O_3$	1 : 1	$BaO{\cdot}Fe_2O_3$	25.0 ($<820°$), 19.0 ($>820°$)[27]
$BaCO_3 + WO_3$	1 : 10	$BaWO_4$	43.6[30]
,,	1 : 1	,,	35.6[29]
$MgO + TiO_2$	1 : 2	$MgO{\cdot}2TiO_2$	36.0

** When a reaction between solid substances takes place smoothly, it must be an exothermic one.

(27) R. Ward and J. D. Struthers, *J. Am. Chem. Soc.*, **59** (1937), 1849.
(28) W. Jander and E. Hoffman, *Z. anorg. allgem. Chem.*, **200** (1931), 245.
(29) W. Jander and W. Stamm, *ibid.*, **190** (1930), 65.
(30) W. Jander, *ibid.*, **166** (1927), 31.
(31) *Cf.* W. Jost, *loc. cit.*, 131.

Summary.

(1) It has been confirmed that three titanates, i.e., magnesium orthotitanate ($2MgO \cdot TiO_2$), metatitanate ($MgO \cdot TiO_2$) and dititanate ($MgO \cdot 2TiO_2$), are formed by the solid reaction between MgO and TiO_2; $2MgO \cdot TiO_2$ is soluble in 4 N HCl and $MgO \cdot TiO_2$ in 12 N HCl, while $MgO \cdot 2TiO_2$ is scarcely soluble even in 12 N HCl.

(2) By following the course of the reaction analytically, it has been found that the first reaction product is $MgO \cdot 2TiO_2$, whatever the mixing ratio of the two components may be; $MgO \cdot TiO_2$ is formed gradually when an excess of MgO is present; and $2MgO \cdot TiO_2$ is formed similarly, but with difficulty.

(3) The reaction has been proved to proceed, under various experimental conditions, in the same manner, and $MgO \cdot TiO_2$ can never be regarded as the first reaction product.

(4) The reaction between $MgO \cdot TiO_2$ and TiO_2 to form $MgO \cdot 2TiO_2$ has taken place more easily than the formation of $MgO \cdot TiO_2$ from $MgO \cdot 2TiO_2$ and MgO.

(5) It has been concluded that, although there exists a notable rapid initial reaction, a further reaction is controlled by the diffusion of the two components through the reaction product. The energy of activation of the diffusion process of $MgO \cdot 2TiO_2$ formation has been estimated to be 36.0 Kilocalories per mole.

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